OPERATOR TRAINING SIMULATOR USING PLANTWIDE CONTROL FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

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OPERATOR TRAINING SIMULATOR USING PLANTWIDE CONTROL FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

by

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LIST OF ABBREVIATIONS

APC	Advanced process controllers
APD	Aspen Plus Dynamics
AVR	Augmented Virtual Reality
ASTM	American society for testing and materials
CAPD	Computer-aided process design
CAPE	Computer-aided process engineering
CC	Cohen and Coon
CDOF	Control degrees of freedom
COM	Cost of manufacturing
CPO	Crude palm oil
CSTR	Continuous stirred tank reactor
CV	Controlled variable
DCS	Distributed control system
DDE	Dynamic data exchange
DDS	Dynamic disturbance sensitivity
DE	Differential evolution
DG	Diglyceides
DO	Dissolved oxygen
DPT	Deviation from the production target
DME	Dimethyl ether
EMOO	Excel-based multi-objective optimization
ERGA	Effective relative gain array
EA	Evolutionary algorithm
FAME	Fatty acid methyl esters
FCI	Fixed capital investment

FFA	Free fatty acid
FHA	Functional hazard analysis
FOPTD	First order plus time delay
GA	Genetic algorithm
GAMS	General algebraic modeling system
GUI	Graphical user interface
HAZOP	Hazard and operability
HAD	Hydro-dealkylation
HDE	Hybrid differential evolution
HE	Heat exchanger
HMI	Human-machine interface
HRA	Human reliability analysis
HPDB	Human performance database
kt	kilotonne
ID	Internal diameter
IFSH	Integrated framework of simulation and heuristics
IFSHO	Integrated framework of simulation, heuristics and optimization
IPC	Industrial PC and intelligent control
INTEMOR	Intelligent industrial real-time on-line process information system
LCA	Life cycle assessment
LLE	Liquid-liquid equilibrium
MINLP	Mixed integer nonlinear programming
MOEA	Multi-objective evolutionary algorithms
MG	Monoglycerides
MPC	Model predictive control
MOO	Multi-objective optimization

MTBE	Methyl tertiary butyl ether
MV	Manipulated variable
NI	Niederlinski index
NPV	Net present value
NSGA II	Nondominated sorting genetic algorithm II
OMBA	Online model-based applications
OLE	Object linking or embedding
OPC	Object Linking and Embedding for Process Control
OTS	Operator training simulator
PFD	Process flow diagram
PID	Proportional-integral-derivative
PLC	Programmable logic controller
PMBR	Pebble bed modular reactor
PWC	Plantwide control
QEM	Quality evaluation module
RBD	Refined, bleached and deodorized
RGA	Relative gain array
RKS EOS	Redlich-Kwong-Soave equation of state
RR	Reflux ratio
RSM	Response surface methodology
SCADA	Supervisory control and data acquisition
SEM	Sequence evaluation module
SIS	Safety instrumented systems
SOC	Self optimizing control
TAME	Tert-amyl methyl ether
TEA	Task evaluation algorithm
TF	Transfer function

TG	Triglycerides
TPM	Throughput manipulator
TL	Tyreus-Luyben
TV	Total variation in manipulated variables
UNIFAC	UNIversal QUAsiChemical (UNIQUAC) Functional-group Activity Coefficients
VCM	Vinyl chloride monomer
VLE	Vapor-liquid equilibrium
VOC	Volatile organic compounds
VR	Virtual reality
WCO	Waste cooking oil
WCPO	Waste cooking palm oil
WS	Weighted sum
yOTS	Yonsei operator training system

LIST OF SYMBOLS

C_p	Equipment purchase cost
C_{BM}	Bare module cost
C^0_{BM}	Bare module cost at base conditions
C_{TM}	Total module cost
C_{GR}	Gross roots cost
EN 14214	European Standard that describes the requirements and test methods for FAME
F_{BM}	Bare module factor
Ndom	Number of individuals dominating each individual in the combined population in NSGA II
NP	Number of individuals in NSGA II
P_C	Critical pressure
T_C	Critical temperature
ω	Acentric factor
ϕ	ERGA

SIMULATOR LATIHAN PENGENDALI MENGGUNAKAN KAWALAN LOJI LEBAR UNTUK PENGHASILAN BIODIESEL DARIPADA SISA MINYAK MEMASAK

ABSTRAK

Kajian ini bertujuan untuk membangunkan simulator latihan operator (OTS) untuk mangkin homogen bagi proses dua langkah biodiesel yang kompleks. Latihan sambil bekerja selalunya memerlukan kos yang tinggi, berisiko dan tidak lengkap kerana beberapa situasi kecemasan mungkin tidak berlaku semasa sesi latihan. Biodiesel dilihat sebagai sumber bahan api alternative, Disebabkan ketersediaan yang terhad sumber tenaga yang tidak boleh diperbaharui dan juga kebimbangan terhadap alam sekitar. Walau bagaimanapun, kos pengeluaran yang tinggi bagi biodiesel menghadkan pengeluaran dan penggunaannya. Salah satu pilihan yang terbaik adalah dengan menggunakan sisa minyak masak (WCO) sebagai sumber bahan mentah bagi pengeluaran biodiesel yang kos efektif dan juga penggunaan WCO yang berkesan. Dalam kajian ini, sisa minyak sawit masak dianggap dengan 6% asid lemak bebas (FFA) sebagai bekalan simpanan. Dua proses pengeluaran biodiesel (kedua-duanya melibatkan pengesteran asid dan transesterifikasi alkali) telah dibandingkan untuk analisis ekonomi dan alam sekitar. Pertama, proses ini dalam simulator Aspen Plus. Selepas itu, kedua-dua proses dioptimumkan dengan mengambil kira keuntungan, tenaga haba dan bahan buangan organik sebagai objektif, dan menggunakan program berasaskan Excel pengoptimuman multi-objektif (EMOO) untuk pengisihan algoritma genetic elitis tidak dikuasai (NSGA-II). Proses 1 mempunyai tiga reaktor transesterifikasi yang menghasilkan sisa organik jauh lebih rendah (32%),

memerlukan duti haba yang lebih rendah (39%) dan sedikit keuntungan (1.6%) berbanding Proses 2 yang hanya mempunyai satu reaktor transesterifikasi dan juga urutan pemisahan yang berbeza. Sistem kawalan loji lebar (PWC) yang berkesan adalah penting untuk operasi loji biodiesel yang selamat, lancar dan ekonomi. Oleh itu, sistem PWC yang sesuai telah dibangunkan untuk proses biodiesel yang menggunakan simulasi rangka kerja bersepadu dan heuristik (IFSH). Merit utama metodologi IFSH adalah keberkesanan penggunaan proses simulator yang baik dan heuristik dalam membangunkan sistem PWC dan kesederhanaan applikasinya. Akhir sekali, pelaksanaan sistem kawalan yang dibangunkan dinilai dari segi masa penetapan, sisihan daripada sasaran pengeluaran (DPT), dan jumlah variasi keseluruhan (TV) dalam pembolehubah yang dimanipulasi. Penilaian-penilaian prestasi dan keputusan simulasi dinamik menunjukkan bahawa sistem PWC yang dihasilkan adalah stabil, berkesan, dan teguh terhadap beberapa gangguan. Akhir sekali, OTS telah dibangunkan untuk penghasilan biodiesel daripada WCO. Oleh itu, latihan menggunakan OTS adalah penting. OTS telah dibangunkan untuk pengeluaran biodiesel dan telah diapplikasikan dengan beberapa keadaan proses yang tidak normal. Keadaan proses ini boleh dimuatkan dan digunakan pada bila-bila masa untuk melatih operator baru dan sedia ada. Kajian ini adalah yang pertama dibangunkan menggunakan struktur lengkap PWC dan OTS untuk mangkin yang homogeneous bagi dua langkah pengeluaran biodiesel daripada WCO.

OPERATOR TRAINING SIMULATOR USING PLANTWIDE CONTROL FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

ABSTRACT

This study aims at developing an operator training simulator (OTS) for the complex homogeneously catalyzed two-step biodiesel process. On-job training is often costly, risky and incomplete as some emergency situations may not arise during the training session. Therefore, training using an OTS is crucial. Pertaining to the limited availability of non-renewable energy sources and the environmental concerns, biodiesel is considered as a potential alternative fuel. However, the high production cost of biodiesel limits its manufacture and utilization. One attractive option is to use waste cooking oil (WCO) as the feedstock that enables cost effective biodiesel production and also facilitates effective WCO utilization. This study considers waste cooking palm oil with 6% free fatty acids (FFA) as feedstock. Two biodiesel production processes (both involving acid esterification and alkali transesterification) are compared for economic and environmental objectives. Firstly, these processes are simulated realistically in Aspen Plus simulator. Subsequently, both the processes are optimized considering profit, heat duty and organic waste as objectives, and using an Excel-based multi-objective optimization (EMOO) program for the elitist non-dominated sorting genetic algorithm (NSGA-II). Process 1 having three transesterification reactors produces significantly lower organic waste (by 32%), requires lower heat duty (by 39%) and slightly more profitable (by 1.6%) compared to Process 2 having a single transesterification reactor and also a different separation sequence. An effective plantwide control (PWC) system is crucial for the safe,

smooth, and economical operation of a biodiesel plant. Hence, a suitable PWC system is developed for the biodiesel process using the integrated framework of simulation and heuristics (IFSH). The main merits of the IFSH methodology are effective use of rigorous process simulators and heuristics in developing a PWC system and simplicity of application. Later, the performance of the developed control system is assessed in terms of settling time, deviation from the production target (DPT), and overall total variation (TV) in manipulated variables. These performance assessments and the results of dynamic simulations showed that the developed PWC system is stable, effective, and robust in the presence of several disturbances. Finally, an OTS has been developed for the biodiesel production from WCO. The developed OTS for biodiesel production process has been investigated for several abnormal process conditions. These process scenarios can be loaded and utilized at any point in time to train the new and existing operators. This is the first study to develop a complete PWC structure and OTS for a homogeneously catalyzed two-step biodiesel production from WCO.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Alternative fuels are being given significant attention due to the increasingly worrying environmental situation. Biodiesel, an alternative fuel to the petroleum-based diesel, is relatively safe, environment friendly, non-toxic and biodegradable as opposed to petroleum-based diesel (Amani et al., 2014a). Fossil fuels such as petroleum fuels and coal have been the major source of energy. However, their non-renewability, highly polluting nature and diminishing reserves make them unattractive for use in the future. Therefore, energy obtained from renewable sources, such as biodiesel and bioethanol, has gained significance in the past few years. Biodiesel i.e. a mixture of fatty acid methyl esters derived from vegetable oils and animal fats, has physiochemical properties similar to those of petroleum-based diesel. Biodiesel or its blends can be used in conventional diesel engines without any modification or with minimal modification (Ramadhas, 2010). It offers many environmental advantages over petroleum-based diesel, as mentioned in Table 1.1.

There is a growing attention in Malaysia towards the use of palm oil in much required biodiesel production as it is the second largest palm oil producer in the world (MPOB, 2013). Previously, the Malaysian energy policy was focused on the use of oil and gas. However, a policy on Renewable Energy was introduced in year 2001 to find alternatives to existing energy sources (KPPK, 2014).

Table 1.1 Comparison between petroleum-based diesel and biodiesel.

Petroleum-based diesel	**Biodiesel**
Complete combustion	May lead to an incomplete combustion
Does not tend to solidify	Tends to solidify
Good cold flow properties	Poor cold flow properties
Higher carbon monoxide emission	Lower carbon monoxide emission
Higher hydrocarbon emission	Lower hydrocarbon emission
Higher particulate emission	Lower particulate emission
Higher smoke emission	Lower smoke emission
Lower production cost	Higher production cost
Non-biodegradable	Biodegradable
Non-renewable	Renewable
Provides relatively poor performances in engine lubricity compared to biodiesels.	Provides better performances in engine lubricity compared to low sulphur diesel fuels.
Toxic	Non-toxic

According to government's estimation, more than 500 kt/annum of palm biodiesel will be utilized nationwide on B5 mandate (i.e. 95 percent petroleum diesel and 5 percent biofuels). According to Allied Market Research, the global second-generation biofuels (advanced biofuels) market would reach $23.9 billion by 2020, registering a compound annual growth rate of 49.4 percent during 2014-2020 (Allied Marker Research, 2014). Currently, biodiesel reaps the largest market share among all biofuels.

The industrial processes are becoming complex and integrated day by day. Consequently, abnormal situation management have become increasingly important considering safety and economic aspects. For example, it is estimated that avoidable

abnormal situations have an annual impact of over 10 billion USD on the operations of US based petrochemical industry due to production loss, equipment damage, etc (Seborg et al., 2010). Also, Kluge et al. (2014) highlighted the cognitive and teamwork requirements of operators and noted the limits of current training practices compared to the training objectives that need to be achieved individually and as a team. Safe and economical production in the chemical industry requires skilled operators. Hence, the OTS is considered as an alternative and efficient tool to train the operators. The OTS development for biodiesel production from WCO has not been found in the literature. Also, application of Aspen Plus Dynamics (APD) with Aspen OTS Framework in OTS development has not been found in the research articles. This work embarks on using APD with Aspen OTS Framework to develop an OTS for the concerned process.

A suitable and realistic process model is crucial for several engineering studies such as model based sensitivity analysis, multi-objective optimization (MOO), plantwide control (PWC) and operator training simulator (OTS) development. Therefore, the processes for biodiesel production from waste cooking oil (WCO) should be simulated considering detailed constituents of WCO and detailed kinetics (esterification and transesterification are represented by 10 and 96 kinetic reactions, respectively), which is scarce to find in the literature. With increasing economic competition and scarcity of resources, there is greater need for optimization of chemical processes. Biodiesel production from WCO is explained below.

1.2 Biodiesel Production from Waste Cooking Oil

The production of fatty acid methyl ester (i.e. biodiesel) by chemically reacting lipids such as vegetable oil with an alcohol can be used as an alternate to reduce the over-reliance on the petroleum-based diesel. There are four different methods to produce biofuel from bioresources, namely direct use and blending of raw oils, micro-emulsions, thermal cracking and transesterification. Transesterification is the most popular way to produce biodiesel from vegetable oils or animal fats (Ziolkowska, 2014). This reaction can be catalyzed by alkali- or acidic-catalysts. The cost of oil is the major contributor to the cost of biodiesel (Sharma and Rangaiah, 2013b). In view of limited availability of pure vegetable oil and its high cost, use of WCO is a favourable choice. Biodiesel production from WCO is attractive for both economic and environmental reasons since WCO is cheaper than vegetable oils and its direct disposal to the environment has adverse impacts.

Although transesterification is more efficient and faster with an alkali catalyst compared to an acid catalyst, high amount of free fatty acid (FFA) in WCO produces soap in the presence of an alkali catalyst (Canakci and Van Gerpen, 2001). Hence, alkali-catalyzed process cannot directly be used to produce biodiesel from WCO. To increase the formation of fatty acid methyl esters (FAME) (i.e., biodiesel) by transesterification, Freedman et al. (1984) recommended using refined vegetable oils with an FFA content lower than 0.5% (w/w), methanol to oil molar ratio of 6:1, and reaction temperature of about 333 K. Also, water content of vegetable oils should be kept below 0.06% (w/w) (Ma et al., 1998). WCO typically contain 2 to 7% of FFAs

(Gerpen, 2005). In these cases, an acid catalyst such as sulfuric acid can be used to esterify FFAs to FAMEs, thus reducing FFA content of feed. Pre-treated oil can then be trans-esterified with an alkali-catalyst to obtain FAMEs. Accordingly, Canakci and Van Gerpen (2001) proposed a two-step process, esterification followed by transesterification, to produce biodiesel. In the view of inevitable need of skilled operators and expensive on-job training, OTS for the complex biodiesel process is essential. Following section describes the OTS.

1.3 Operator Training Simulator (OTS)

Intricate and highly interacting production processes pose tough challenges in maintaining safe and efficient production. An inevitable need of skilled operators to increase the safety and the productivity is not new to the chemical industry. Consequently, the training of operators is considered as a very important activity in the chemical industry. An OTS provides an alternative to train operators without actually endangering the plant and personnel. In complex industries, where safety is paramount, identification of key factors that can degrade/enhance safety is a must (Park et al., 2004). Yang et al. (2001) reported that significant percentage of property losses in the hydrocarbon processing industries is due to operational errors or process upsets. This reinforces the need of OTS to develop and retain the operators' skills. To ensure that operators retain the knowledge, skills and remain competent to control processes in emergency conditions, they should be provided with training opportunities to develop and sustain their capabilities. On-job training is often costly, risky and incomplete as some emergency situations may not arise during the training

session. Therefore, training using an OTS is crucial. Manca et al. (2013) discussed the benefits of integrating and interlinking a dynamic process simulator with a dynamic accident simulator in OTS training. According to Shepherd (1986), as long as operators are working on the complex plants and equipments, development and administration of their training are required. He reported that a training technique implies adopting one or more of the following: teaching plant and process knowledge, on-job instruction, training on a simulated plant and development.

The paradigm of one of these training methods alone may not be effective. Shepherd (1986) recommended adopting all the above mentioned for a comprehensive training program. In the chemical industry, especially in the case of continuous processes, OTS has been used (Balaton et al. 2013). An increasing number of chemical companies use OTS aiming to train the operating staff on handling different malfunctions and infrequently occurring modes of operation. Other applications of OTS include assessment of operators' skills, supporting engineering tasks such as investigating alternate control mechanisms and performing safety tests without any risk to the real system (Fürcht et al. 2008; Rey 2008).

In addition to classroom teaching and field training, simulator training is also significant in the operator training program (Jayanthi et al. 2011). OTS is safe and reliable to train control room operators as long as it can provide a credible simulation of the real plant (Drozdowicz et al. 1987). Figure 1.1 illustrates the comparison between real plant training and simulator training.

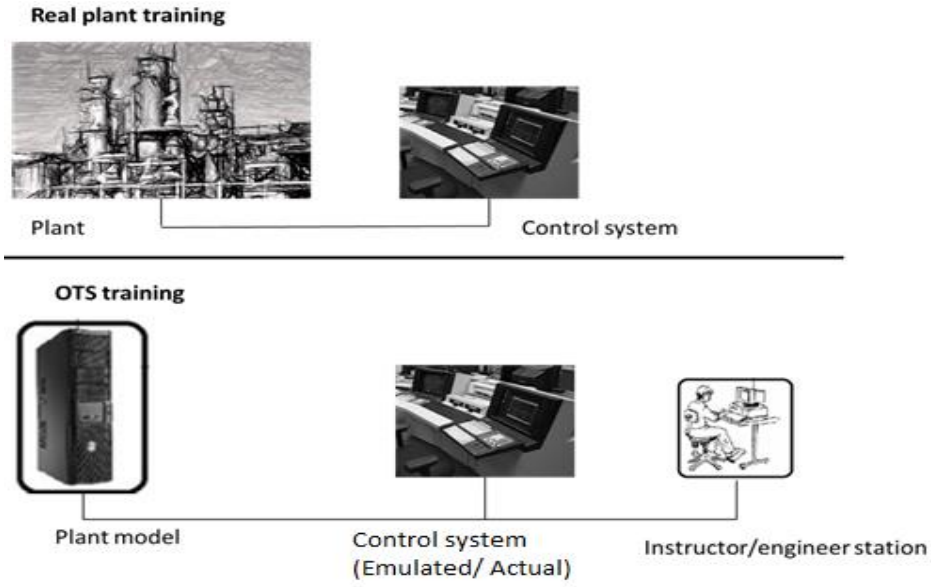

Figure 1.1 Comparison between real plant training (top) and simulator training (bottom).

Typically, the simulator includes a replica of the plant's control room (hardware, interfaces, screens, printers, etc.) and a software emulation of the distributed control system to be coupled with the process models (Spanel et al., 2001). The general configuration of the full scope OTS for any chemical plant can be as shown in Figure 1.2.

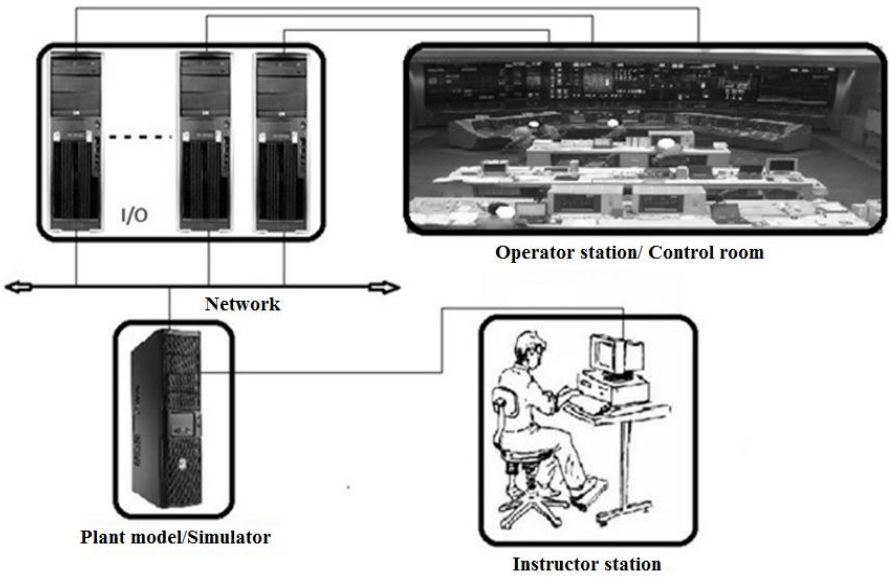

Figure 1.2 General configuration of full scope OTS.

In this figure, the instructor station provides the interface for the instructor to insert faults, monitor and control the training session while the trainee operators use the operator station. The trainee operator station has generic process control system schematics that enable point and click access to the controller faceplates. The instructor station functionalities reported by Dudley et al. (2008) are: scenario creation and imparting malfunctions/upsets into the process model, monitoring and trending of any plant variable, training and evaluation of operators, run/pause/resume and load/save capabilities, Snapshots, backtracks and speed control (i.e. fast/slow capabilities), and storing of data on plant variables, which can be used for post-scenario reviews.

In addition, preliminary hazard and operability study (HAZOP) analysis is carried out to assist a trainee find out causes and possible solutions. HAZOP is a structured and systematic examination of a non-existing or existing process in order to identify and evaluate problems that may indicate risks to process or personnel, or reduce the efficient process operation. OTS needs a suitable process model that can reflect the process as real as possible. Therefore, it is important to carry out a realistic simulation, determine optimal conditions and develop a complete PWC structure. In this work, OTS uses the same process model as it is used in MOO and PWC study. The optimal parameters determined from MOO of the biodiesel process is used in PWC and OTS study. Following section presents the merits of MOO.

1.4 Multi-objective Optimization (MOO)

Once process extablished and simulated, MOO is used to determine the optimal parameters of the decision variables. MOO is also used to compare the two process alternative. In general, MOO is the method of finding optimal values of the parameters for the maximization or the minimization of given objectives within prescribed constraints. MOO involves maximizing or minimizing multiple objective functions subject to a set of constraints, for example analyzing design tradeoffs, selecting optimal product or process designs, or any other application where an optimal solution with tradeoffs between two or more conflicting objectives is desired. Optimization plays crucial role in reducing material and energy requirements as well as the waste formation in chemical processes. It is also essential in determining better design and operation of chemical processes. Many chemical processes involve several objectives, most of which are conflicting in nature. Several chemical processes have many variables with complex inter-relationships; optimizing these objectives is challenging. MOO is needed to determine the optimal solutions in such applications. MOO is used to find a set of nondominated solutions for two or more objectives simultaneously (Sharma and Rangaiah, 2013b). Consequently, in last few years, a significant attention has been given to MOO. MOO has been vastly used to optimize chemical processes having conflicting objectives such as conversion, selectivity, yield, energy, environment and safety in addition to economic objectives. Evolutionary algorithms, such as non-dominated sorting genetic algorithm (NSGA-II), are popular methods to generate Pareto optimal solutions for a multi-objective optimization problem. It is a stochastic optimization method that that generates and uses random variables. Other stochastic optimization

methods include simulated annealing, quatum annealing, swarm algorithms, differential evaluation etc. NSGA-II has become popular approach and it can be seen from its wide applications.

The main advantage of evolutionary algorithms (EA) is that the EAs are inherently stochastic in nature, and thus they generate the Pareto front when applied to solve multi-objective optimization problems. Multi-objective optimization problems can be solved using Genetic algorithm and its improved versions to find set of points on the Pareto front. The major drawbacks of multi-objective evolutionary algorithms (MOEAs), such as NSGA, that use non-dominated sorting and sharing are: (1) their computational complexity $O(MN^3)$ (where, M is the number of objectives and N is the population size), (2) their non-elitism approach (absence of elitism as opposed to NSGA-II, where parents are selected from the population by using binary tournament selection based on the rank and crowding distance), and (3) the necessity to specify a sharing parameter (Deb et al., 2002). Deb et al. (2002) proposed extension of NSGA i.e., NSGA-II, which alleviates all of the above three difficulties; hence, NSGA-II is used later in this study. After finding the better process out of the two alternative processes, a suitable PWC structure should be implemented; this is explained below.

1.5 Plantwide Control (PWC)

After the best process is identified based on the optimization results, PWC structure is developed for the chosen process. Generally, chemical processes consist

of a several integrated unit operations. These material and energy integration make the process complex. Besides, most chemical processes are non-linear in nature. The main objective of PWC is to synthesize a control structure that leads to smooth, safe and economic operation of the entire plant. Because of market competition, dictated by changing customers' demand, efficient operation of plant is crucial. Material and energy recycles are constantly employed to improve economics. The presence of recycle streams alters the process dynamics that then leads control problems. Also, tough safety norms and stringent environmental regulations demand an effective PWC system.

Merits of PWC over normal unit-wise control are (i) complete PWC perspective is considered which is important due to several interacting process operations (ii) decisions are taken systematically based on the hierarchy of preferences e.g. control objectives, product quality, throughput manipulator (TPM), process constraints, safety constraints, inventory etc (iii) location of TPM, which is critical in PWC system, is properly identified and (iv) critical issues can be categorically evaluated such as snowball effect, slowing dynamics due to the recycles, propagation of disturbances in the multiunit process etc (Seborg et al., 2010). In case of any discrepancy regarding the loop pairings, control loop pairing arrived from the PWC method should be preferred over the decision arrived from the base layer control method. So far, many systematic PWC methodologies have been developed. Each of the methodologies offer some advantages as well as some limitations due to the particular approach followed. It is worth noting that different methodologies may yield different control structures, and hence the different control performance. Based on specific requirements, a particular methodology can be

adopted. To circumvent these challenges of the PWC problem, some potential methodologies have appeared in recent years. To circumvent overreliance of other PWC methodologies on heurisics, Murthy Konda et al. (2005) proposed the integrated framework of simulation and heuristics (IFSH) that combines the benefits of process simulators as well as heuristics. Optimization and mathematical-based approaches usually depend on process models and involve intensive computations. For examples, Zhu et al. (2002) proposed optimization-based strategy to integrate linear and non-linear model predictive control. These approaches are often prone to model inaccuracies. Mixed-approaches combine any of the heuristics, optimization or mathematical methods. One of such methodologies is the self-optimizing control (SOC) proposed by Skogestad (2004). The core of this methodology is to find a set of self-optimizing variables, which when maintained constant leads to minimal loss in the profit as and when disturbances occur, without the need for re-optimization as these variables keep the plant 'near-optimal'. Subsequent section presents the problem statement that established .

1.6 Problem Statement

Finite availability, strict environmental regulations and fluctuating fuel cost are the main factors behind increasing focus on the alternative fuels. Given the merits of the biodiesel, it is considered as the one of the most promishing alternative fuels. Biodiesel produced from edible vegetable oil has many demerits, such as high cost of biodiesel production and fuel vs food issue. As the consequence, use of WCO is found to be favourable as it is cheaper than pure oil. As the significant percentage of

property losses in the hydrocarbon processing industries are found to be due to operational errors or process upsets, well trained operators are inevitable for the safe and efficient process operation. In addition, the rate of accidents arising form operators' errors is relatively more in Malaysia as compared to the rates in developed nations. Conventional training methodologies, such as the training of the new operators in existing plants by allowing them to work with experienced operators in front of actual control panel, do not impart enough skills to the operators when dealing with infrequent critical conditions.Hence, an OTS is essential for the effective operator training.

In essence, to make OTS realistic and effective, the realistic process model operating at the real optimal conditions and having an effective PWC system is crucial. In addition. to obtain increased profitability with the least use of resources, optimization of process for many conflicting objectives is important. Also, safe and efficient operation of a biodiesel process inevitably requires an effective PWC structure. Hence, MOO and PWC study are important for the OTS. Based on these issues, following objectives are formulated.

1.7 Objectives

The main objective of this research is to develop an OTS for the biodiesel process. Important subsections of this research are simulation, MOO and PWC for biodiesel production from WCO. The elaborate objectives of this research are as follows:

1. To develop a steady state simulation for palm oil based biodiesel production from waste cooking oil.
2. To carry out an excel based evolutionary multi-objective optimization to compare the two alternative proceeses for the optimal parameters.
3. To develop a dynamic simulation to study the transients of the process.
4. To apply a suitable PWC strategy to the chosen biodiesel process.
5. To develop an OTS to train the operators for enhancing their skills and ability to deal with critical and emergency operations.

1.8 Scope of Study

The main aim of this study is to develop an OTS for the complex biodiesel process. This is the first study to investigate the application of the commonly used Aspen Plus Dynamics in the OTS development for the homogeneously catalyzed biodiesel production from WCO. Experience from this is useful for development of OTS for other complex processes, and thus leading to the increased operator training for safer plant operations. Complex processes, such as biodiesel production from WCO, require skilled operator to maintain the safety and productivity of the biodiesel process. Using WCO for biodiesel production enables cost effective biodiesel production and also facilitates effective WCO utilization. As an effective OTS requires a realistic process model, firstly in this study, two alternative biodiesel processes are optimized using NSGA-II and compared based on economic and environmental criteria. Both the process alternatives use alkali-catalyzed transesterification, which is more efficient and also used in industrial practice. Optimization study determines the optimal parameters, such as temperature,

residence time and feed location, to make process more profitable and less damaging to the environment. Later, an effective PWC system is developed for the better process using IFSH methodology, which makes effective use of process simulators as well as heuristics. The performance of the developed PWC system is investigated using several performance assessment criteria. These performance assessments and results of dynamics simulations indicate that the developed PWC system is stable, effective and robust in the presence of several disturbances, and that biodiesel quality is maintained despite these disturbances. Finally, an OTS has been developed for biodiesel production from WCO. The developed standalone OTS for biodiesel production has been investigated for several abnormal process conditions, each of which can be inserted by an Instructor at will. These scenarios can be replayed as and when the operators require. Next section describes the organization of the thesis.

1.9 Organization of Thesis

This thesis comprises of five major chapters. Each chapter has been explained in detail with the following contents.

Chapter 1 elaborates on the background information about this research, the significance of this research and the techniques being followed to achieve the desired objectives. The objectives are chosen so as to provide a significant breakthrough in this field of research. This chapter also briefly explains the MOO, PWC and OTS with respect to chemical processes, in general.

Chapter 2 discusses and reviews extensively about MOO, PWC and OTS for a homogeneously catalyzed biodiesel process. Detailed reviews about the application of MOO, PWC and OTS in various chemical processes have been also carried out.

Chapter 3 presents the methodology carried out in this research. This chapter consists of four major parts. The first part explains the design and simulation of two alternative biodiesel processes. This is followed by MOO for different conflicting objectives using an Excel-based multi-objective optimization (EMOO) program for the elitist NSGA-II. Later, a suitable PWC structure is developed for the process using IFSH methodology. Finally, an OTS is developed for the process using APD with Aspen OTS Framework on top.

Chapter 4 details the results and discussion obtained from simulation, MOO, PWC and OTS. Two alternative processes are compared based on several criteria, namely profit, heat duty and organic waste. Nextly, the employed PWC system is investigated for different criteria, namely settling time, dynamic economic index based on deviation from the production target (DPT) and total variation (TV) in manipulated variables. Finally, the developed standalone OTS for biodiesel process has been investigated for several abnormal process conditions, each of which can be inserted by an instructor. These include: equipment malfunctions, utility failures, fire, pressure safety valves and development of startup procedures resulting in reduction of production time and loss.

Chapter 5 finishes off with the conclusions that have been arrived from this work. In addition, the future directions of this research have been established.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

As the main goal of this work is the OTS development for biodiesel process that require a MOO and PWC study, recent research works in the field of biodiesel production, MOO, PWC and OTS development are reported in this chapter. Relevant and recent previous research works relating to these areas discussed and presented in systematically. The objectives of this research are based on the gaps determined from the careful analysis of the previous studies. Literature study shows that increasing number of chemical industries is looking to use OTS to train their operators given the benefits of OTS.

Biodiesel production from WCO is beneficial because the WCO is cheaper and utilizing it for the fuel production avoids its wastage. This, consequently, avoids the pollution as the WCO would have to be dumped, which would cause environmental degradation, e.g. water pollution causing main threat to the aquatic animals. Biodiesel production from pure vegetable oil is feasible. However, it has two major drawbacks: high cost and limited availability. After establishing the raw material for biodiesel production, suitable process design should be established. Successively, optimal design and operation parameters should be identified to run the process optimally. MOO can play an important role as it has the ability to find the optimal condition for the complete plant condidesring multiple objectives. Safe,

robust and proficient process operation requires an effective PWC system, especially when the process is as complex as the homogeously catalysed two step biodiesel production from WCO. Information is presented in tabular form, wherever required, to understand the highlights and gaps in the previous studies. Relevant previous studies are then critically analyzed.

2.2 Biodiesel Production from Waste Cooking Oil (WCO)

Biodiesel i.e. FAME derived from vegetable oils and animal fats, has physiochemical properties similar to those of petroleum-based diesel. Biodiesel offers has many advantages over petroleum-based diesel fuel such as a higher cetane number, no aromatics or sulphur compounds, and reduced emission of carbon dioxide, carbon monoxide, hydrocarbons and particulates in the exhaust gas (Ramadhas, 2010). Pure biodiesel or its blend with petroleum-based diesel can be used in the existing diesel engines with either no or slight modifications (Ramadhas, 2010). The non-renewability, adverse environmental impacts and increasingly diminishing reserves of current fuels make researchers to look for alternative fuels. Among such alternative fuels, biofuels (e.g. biodiesel) have gained significant attention in the past few years.

Biodiesel can be produced through micro-emulsions, thermal cracking and transesterification. Among these routes, transesterification is the most popular way to produce biodiesel as it is more efficient and has moderate operating conditions. Transesterification reaction is reversible, and can be catalysed by alkali/acid homogeneous catalyst, heterogeneous catalyst as well as enzymes (Ramadhas, 2010).

Also, a non-catalytic route using supercritical methanol can be adopted (Kusdiana and Saka, 2001). However, these studies are still in the developmental phases, and are not being used commercially. Many researchers (Zhang et al., 2003a; Zhang et al., 2003b; Haas et al., 2006; West et al., 2008; Myint and El-Halwagi, 2009; Santana et al., 2010) have studies the techno-economic feasibility of different transesterification methods. They concluded that the price of the feed oil is the largest contributor to the cost of biodiesel production.

Zhang et al. (2003a) proposed four biodiesel production processes namely, alkali-catalyzed process using pure vegetable oil, alkali-catalyzed process using WCO, acid-catalyzed process using WCO, and acid-catalyzed process using hexane extraction. Later, Zhang et al. (2003b) performed economic analysis and found that the acid-catalyzed process using WCO is more economical compared to others studied. West et al. (2008) conducted economic analysis of four biodiesel production processes, using WCO as feedstock; these include acid-catalyzed, alkali-catalyzed, heterogeneous acid-catalyzed and supercritical processes. They concluded that heterogeneous acid-catalyzed process is more economical than others, but it is still in the development phase. Catalyst deactivation and their selectivity towards the biodiesel are mong the maor challenges. Talebian-Kiakalaieh (2013) reported that utilization of waste cooking oil can reduce biodiesel production cost by 60-90%. Development of kinetics for the transesterification reaction has been studied previously (Freedman et al., 1986; Nourreddini and Zhu, 1997; Kusdiana and Saka, 2001; Jain and Sharma, 2010). Significant attention is also being given to the use of heterogeneous catalysts in biodiesel production (Sharma et al., 2011; Amani et al., 2014b; Wijaya et al., 2013).

Biodiesel production using homogeneously catalyzed transesterification is the most popular method used in the industries (Zhang et al., 2003a; Nazir et al., 2009; Lurgi, 2013; Platinumgroup, 2013). Transesterification reaction is faster and requires smaller methanol-oil ratio as compared to acid transesterification (Freedman et al., 1986) under moderate operating conditions. While alkali-catalysed route is widely accepted, it has the disadvantage of low tolerance of water and FFA in the feed. Use of pure oil that offers low content of water and FFA lead to expensive biodiesel production that is incompetent against existing fuels. Using WCO for biodiesel reduces the cost of production significantly; but it normally has higher FFA content. If the feed contains higher levels of water and FFA than the maximum tolerance level, a pre-treatment section is required to convert FFA into biodiesel. In homogeneous biodiesel production, researchers have used different separation sequences. Myint and El-Halwagi (2009) studied these alternative sequences technically and scientifically. Application of different unit operations has also been tested. For example, Apostolakou et al. (2009) proposed phase separation between biodiesel and glycerol by a centrifuge separator as opposed to the application of a decanter by Myint and El-Halwagi (2009).

In summary, the limited availability of pure vegetable oil and its high cost, using WCO for biodiesel production is a beneficial. Biodiesel production from WCO is attractive for both economic and environmental reasons since WCO is cheaper than vegetable oils and its direct disposal to the environment has adverse impacts. Other research on the development of novel reactor designs for biodiesel production includes: membrane reactors (Dube et a., 2007), gas–liquid reactors (Behzadi and Farid, 2009) and rotating packed reactors (Chen et al., 2010); however, these are still

under developmental phase. Next subsection presents the information on MOO for the chemical processes.

2.3 Process Design and Multi-objective Optimization (MOO)

In a chemical process, raw materials are transferred into the desired products through series of processing steps. In essence, chemical process design involves (1) selection of individual transformation steps and (2) interconnection of these transformation steps to form a complete process that can produce the desired output.

2.3.1 Process Design

Process design is a structured approach to improve tangible benefits such as cost reduction and increase in the process efficiency. Sieder et al. (2010) proposed the general steps to be followed in process design. Firstly, a primitive problem is developed. Then base case is developed after the feasibility study. In parallel, algorithmic methods (e.g. to synthesize reactor-separator-reactor (R-S-R) network) are employed to find the better process flowsheet. Sequencing of unit operations, material/energy recycles and heat integration are decided upon at this stage. Also, plantwide controllability is assessed simultaneously. Later, a detailed design, equipment sizing and optimal design using optimization (e.g. based on profitability analysis) is carried out. Peters and Timmerhaus (2002) presented graphical and analytical method for optimum design.

Sinnott et al. (2008) proposed the steps for the process design as design objectives, setting design basis, generation of possible designs, fitness testing, economic evaluation using & optimization, detailed design & equipment selection, and construction & operation. Ray and Sneesby (1998) presented the steps of process design: conception and definition, flowsheet development, design of equipment, economic analysis, optimization and reporting. Biegler et al (1997) reported the optimization approaches to the process design which rely on the optimization techniques such as missed-integer optimization methods.

Myint and El-Halwagi (2009) adopted the following approach for the biodiesel process design. This approach includes (1) synthesis of a base-case flowsheet, (2) simulation of the base case and selection of appropriate thermodynamic databases, (3) identifying opportunities for process integration and cost minimization, (4) development of a plantwide simulation of the process with various mass and energy integrations, and (5) cost estimation and sensitivity analysis. Datta (2008) presented the process design and engineering using visual basic application. Chemical process design requires the selection of a series of processing steps and their integration to form a complete manufacturing system (Smith, 2005). There are two approaches for process design, namely building an irreducible structure, and creating & optimizing a reducible structure. Former has many drawbacks such as several possible designs must be evaluated and evaluating many designs may not ensure the best design. On the other hand, later approach is a superstructure i.e hyperstructure embedded within it all feasible process operations and feasible interconnections that are candidates for an optimal design (smith, 2005). Smith (2005) followed an onion approach where design is started with the reactor.

Then separation train is decided and recycles are connected. Later, possibility of heat recovery is explored and need of external hear utility is studid. Algorithm methods are used for the detailed process design, synthesis of chemical reactor networks, separation train synthesis, R-S-R network synthesis and heat & mass exchange network synthesis. Several possible design are studied and compared using the algorithm based on predecided criteria. The optimization approach for the process design are applied at the later stages when preliminary designs are assessed. Next section discusses the MOO.

2.3.2 Multi-objective Optimization (MOO)

MOO is the method that is used to simultaneously optimize multiple objectives that often exhibit the trade-off. In view of the increasing economic competition and paucity of resources, there is larger need for optimization of chemical processes. Chemical processes are optimized for selected objectives with respect to relevant design and operation variables. Chemical processes are often encountered with conflicting objectives, for example profit vs capital investment. Until the end of the last century, economic criteria (e.g. cost or profit) were commonly used for optimizing process design and operation. However, in the last decade, MOO has been used increasingly to optimize chemical processes for contradictory objectives such as conversion, selectivity and yield in addition to economic criteria (Sharma and Rangaiah, 2013a). Eventually, several other performance criteria such as energy, environment and safety are receiving substantial attention in process design and operation optimization. Applications of MOO in chemical processes are presented below.

2.3.2 (a) Multi-objective Optimization of Chemical Processes

MOO has been extensively used in the chemical processes, such as petroleum refining, petrochemicals, polymers, parameter estimation, power sector, renewable energy, carbon capture, biotechnology, food and pharmaceuticals. In this section, recent applications of MOO in the biodiesel process is presented in Table 2.1. Bhaskar et al. (2000) have reviewed the applications of MOO approach in chemical engineering. (They summarized these MOO applications under five categories, namely process design and operation, petroleum refining and petrochemicals, biotechnology and food technology, pharmaceuticals, and polymerization. They mentioned that use of MOO in chemical engineering has increased between the years 2003 and 2007). Sharma and Rangaiah (2013a) reviewed the articles on MOO from 2007 to mid-2012. From their review, it can be observed that NSGA-II and related stochastic algorithms have been commonly used by the researchers to determine the optimal operating and design parameters for the processes considering the manifold objectives.

Myint and El-Halwagi (2009) studied four alkali-catalyzed biodiesel processes having different separation sequences and found that biodiesel and glycerol separation should be performed first, followed by methanol recovery and water washing. They studies the design, analysis, and optimization of biodiesel production from soybean oil. Four process flowsheets are synthesized to account for different separation sequences. The performance of these flowsheets, along with the key design and operating criteria, are identified by conducting the simulation

experiments using Aspen Plus. However, they have not considered the detailed kinetics of the reactions.

Table 2.1 Recent applications of MOO in biodiesel production.

	Application	**Objectives**	**Optimization technique**	**Reference**
1	Biodiesel Production from Cooking Oil and Algae	Max: Biodiesel yield; Min: Water requirement	MINLP and RSM	Martin and Grossmann (2012)
2	Biodiesel production from pure oil	Max: Product purity; Min: Energy	Genetic algorithm (GA)	Nicola et al. (2010)
3	Biodiesel and chemicals from rapeseed oil	Max: Net present value (NPV); Min: environmental impact	ε-constraint	Vlysidis et al. (2011)
4	Biodiesel process from WCO	Max: profit; Min: fixed capital Investment; Min: organic waste	DE	Sharma and Rangaiah (2013b)
5	Biodiesel process from pure oil i.e single triglyceride	Max: Profit; Min: volatile organic compounds (VOC) emissions; Max: number of chemical operators' jobs	GA	Woinaroschy (2014)

Nicola et al. (2010) optimized two slightly different alkali-catalyzed biodiesel processes for energy consumption and product quality. They used genetic algorithm to minimize energy requirement and maximize the biodiesel purity. However, rather than taking biodiesel purity as the objectives, considering it as the constraint in the constrained MOO is more useful. This is because the biodiesel purity has to be just maintained above the EN or ASTM standards, and not to maximize it. However, they also represented the oil as just a triglyceride.

Martin and Grossmann (2012) carried out simultaneous optimization and heat integration of different technologies for the transesterification of oil. They considered five different technologies for the transesterification of the oil (viz. homogeneous acid- or alkali-catalyzed, heterogeneous basic-catalyzed, enzymatic, and supercritical uncatalyzed). They formulated the problem as a mixed integer nonlinear programming (MINLP) problem where the models for each of the reactors are based on surface response methodology to capture the effects of the variables on the yield. Simultaneous optimization and heat integration for the production of biodiesel from each of the different oil sources in terms of the technology and the operating conditions, is studied. They found that the optimal conditions in the reactors differ from those traditionally used because of the consideration of the separation tasks. They have also not considered the details compostion of oil and detailed kinetics of the reactions. Vlysidis et al. (2011) used ε-constraint method to optimize the biodiesel production form rapeseed oil. They maximized net present value (NPV) and minimized the environmental impacts.

Sharma and Rangaiah (2013b) optimized biodiesel production from WCO for multiple objectives, using multi-objective differential evolution. They considered both esterification and transesterification steps, and three continuous stirred tank reactors (CSTR) in series for transesterification, which has obvious advantages. They considered profit (maximize), capital investment (minimize) and organic waste (minimize) as the objectives. However, they represented the WCO by just one fatty acid and one triglyceride. Woinaroschy (2014) optimized the Biodiesel process considering profit (maximize) and volatile organic compounds (minimize) as the objectives. They used genertic algorithm to obtain the Pareto-optimal front. This work also does not consider the detailed kinetics of the reactions and detailedconstituents of the oil. Huerga et al. (2014) presented an integrated process to obtain biofuels from Jatropha curcas crop. They performed several experiments to optimize the process diminishing the consumption of methanol and catalysts. Fauzi and Amin (2013) optimized oleic acid esterification catalyzed by ionic liquid. They used RSM based on central composite design for single-objective optimization, while artificial neural network with genetic algorithm was employed for simultaneous optimization of responses to the reaction conditions. Rahimi et al. (2014) studied the optimization of biodiesel production from soybean oil in a microreactor. They used Box-Behnken method and RSM for the optimization of molar ratio of methanol to oil, catalyst concentration and temperature. Rincón et al. (2015) optimized the Colombian biodiesel supply chain from oil palm crop based on techno-economical and environmental criteria.

Mendoza et al. (2015) proposed an integrated and generic framework for eco-design that generalizes, automates and optimizes the evaluation of the environmental

criteria at earlier design stage. The approach consists of three main stages: first two steps correspond to process inventory analysis based on mass and energy balances and impact assessment phases of Life cycle assessment (LCA) methodology, the third stage of the methodology is based on the interaction of the previous steps with process simulation for environmental impact assessment and cost estimation and the use of multiobjective optimization. They illustrated this methodology through the acid-catalyzed biodiesel production process.

In conclusion, it can be noticed from the Table 2.1 that detailed esterification and transesterification kinetics have not been considered for the homogeneously catalyzed two-step biodiesel production from WCO. Previous studies (Morais et al., 2010; Zhang et al., 2003a; Zhang et al., 2003b; West et al., 2008; Sharma et al., 2013; West et al., 2007; Kiss et al., 2012) use a single triglyceride/FFA and FAME to represent the vegetable oil and biodiesel, respectively. In addition, fixed conversions of FFA and triglyceride into FAME were often assumed (Morais et al., 2010; Zhang et al., 2003a; Zhang et al., 2003b; West et al., 2007). These should be avoided in order to obtain more realistic outcomes, particularly for comparing plant performance for various feedstocks. In this direction, Garcia et al. (2010) considered three triglycerides to represent vegetable oil, but mono- and di-glyceride intermediates were neglected in the reaction. Also, it can be noticed from Table 2.1 that NSGA-II has not beed used for the optimization of the homogeneously catalyzed two-step biodiesel production, thus far. Merits of NSGA-II are discussed below.

2.3.2 (b) Nondominated Sorting Genetic Algorithm II (NSGA-II)

In general, MOO techniques can be classified into three techniques: (i) generating techniques, (ii) techniques which rely on prior articulation of trade-offs or preferences and (iii) interactive techniques which rely on progressive articulation of preferences (Sharma et al., 2012). Generating techniques (or a posteriori preference articulation methods) search for many Pareto-optimal solutions before deciding on trade-offs. The NSGA-II is an example of generating techniques. On the contrast, a priori preference articulation techniques require decisions on trade-offs before searching for the corresponding Pareto-optimal solution. Prior articulation method reduces the MOO problem into a single-objective problem which can be solved with single-objective optimization strategies. However, this requires deep knowledge which may not be available in every case. The generating techniques, in which there is no possible reduction of complexity of the search space due to the absence of input of decision maker, circumvent this short coming. Interactive methods combine the strengths and weaknesses of both methods. Srinivas and Deb (1995) proposed NSGA based on genetic algorithm for MOO that is based in natural selection (i.e. random population generation, selection, cross-over, combination, mutation etc.). It was then improved by introducing elitism by Deb et al. (2002), which they called it as an elitist NSGA or NSGA-II. Elitism is when the parents are selected from the population by using binary tournament selection based on the rank and crowding distance in the elitist NSGA. NSGA-II is superior to earlier genetic algorithm in terms of the following: fast non-dominated sorting for population sorting based on Pareto dominance and the crowding distance assignment for calculating the density measure. More information about NSGA-II can be found in Deb et al. (2002). It can

be seen from the literature review, NSGA-II has not been applied to the biodiesel processes. Next subsection describes the PWC methodology.

2.4 Plantwide Control (PWC)

PWC refers to the design of a control structure for the complete process having interconnected unit operations with mass and/or energy recycles. Material and energy recycles change the process dynamics by introducing an integrating effect, which can lead to the snowball effect (i.e., high sensitivity of recycles to disturbances). A good control system distributes the effect of disturbance(s) to unit operations involved to avoid severe snowball effect. PWC system design for safe, stable, and efficient operation of complex chemical processes have been studied extensively (Luyben et al., 1997; Zhu and Henson, 2002; Herrmann et al., 2003; Al-Arfaj and Luyben, 2004; Araújo et al., 2007; Vasudevan et al., 2009a; Vasudevanand Rangaiah, 2011). Vasudevan et al. (2009a) have systematically classified the PWC methodologies. Structure-based classification put methodologies to centralized, decentralized and mixed methods, while approach-based classification classify methodologies into heuristic, optimization, mathematical and mixed-approach categories. By and large, heuristic-based approach is largely dependent on the experience. These methodologies generally use traditional PID controllers to achieve a stable control structure with good performance with a relatively uncomplicated procedure. For example, Luyben et al. (1998) proposed one such methodology that has nine-steps based on heuristic. Although this methodology has been proven to yield a stable PWC for many processes, it has a major drawback of its overreliance on heuristics as heuristics may always not be applicable to each process.

Methodologies in these studies can be categorized into heuristics, optimization, mathematical, and mixed approaches (Vasudevan et al., 2009b).

The rigorous mathematical and optimization based methodologies are complicated and require extensive computations especially for complex chemical processes. Additionally, their solutions depend on the degree of details used. Therefore, heuristic based methodologies seem to be attractive as they are less complicated and easy to implement. However, heuristic based methods largely depend on experience, and do not extract the advantages of the rigorous process simulators while designing a control structure. For example, rigorous process simulators can be effectively used to aid in decision making in selecting suitable controlled variable (CV) and manipulated variable (MV) pairings keeping in mind the PWC perspective, such as product quality, throughput and inventory control. IFSH methodology (Herrmann et al., 2003; Vasudevanand Rangaiah, 2011; Vasudevan et al., 2009b) makes effective use of the rigorous process simulators. Another PWC methodology is economic plantwide control/self-optimizing control (SOC) (Skogestad, 2004; Jagtap et al., 2011; Skogestad, 2012). IFSH methodology is attractive as it is easy to implement, and involves minimal computations other than process simulation. Zhang (2011) performed a comparative study of implementation of IFSH and SOC to the ammonia process. They found that (i) settling time is reasonable for both methods; however, process settled faster when IFSH is used, (ii) IFSH has smaller accumulation, (iii) DPT is also smaller when IFSH is used and (iv) SOC yielded slightly better steady state profit.

Of late, integrated design and control methods have received substantial prominence as controllability of the process is inheritantly included such methods. This can be achieved by adopting either simultaneous or sequential approach. A main merit of simultaneous approach is that it takes in to consideration the design as well as control perspectives simultaneously. This yields the most optimal design and control for the process. However, this method has severe disadvantages, such as (i) extreme computation load due to the large search space when the design and control problems are combined and (ii) model simplifications and approximations are often required, and hence inaccuracy is an inherent disadvantage (Zhang, 2011). On the other hand, sequencial approach is simple and computationally less expensive. However, the associated drawback of this methodology is that it may not yield the best possible design and control as many design alternatives may not have been considered in the first place. Next best solution to circumvent this challenge is to use a modified sequencial approach, in which several possible design alternatives are to be investigated prior to the control and then the control solution to be employed on the chosen design(s). PWC of several chemical processes is presented in the following subsection.

2.4.2 Plantwide Control (PWC) of Chemical Processes

At first, Buckley (1964) studies the PWC system design in 1964. In past few decades, PWC has been actively studied as the result of increasing focus on the controllability of the process in the presence of the intensive material and heat intergration. PWC is crucial for the safe and efficient operation of chemical processes. Accordingly, researchers have focused on developments of many PWC

methods and applied to several chemical processes. Several systematic PWC system design methodologies have been developed in the recent past. Vasudevan et al. (2009b) carried out a systematic review and classification of these methodologies. PWC methodologies can be classified on the basis of their approach, such as heuristics-based, mathematics-based, optimization-based band mixed approaches.

Different processes may exhibit distinct characteristics that may pose different challenges in process control. For instance, a highly exothermic/endothermic process may require more rigorous temperature control than that for an isothermal process, reactor with possibility of side reaction may require precise temperature control than that for a normal reactor, process with several recycles may exhibit snowball effect as opposed to the simple process and a highly coupled distillation column may require more complex control structure than that for a non-coupled column. Table 2.2a lists the recent applications of PWC in biodiesel production processes.

Shen et al. (2011) explored the design and control of biodiesel process with phase segregation and recycle in the reactor system. They proposed a decentralized control structure and satisfactorily tested for 20% production rate change with a settling time of less than 10 h. They obtained a 20% reduction in the total annual cost and 26% reduction in the energy cost using internally recycled glycerol. However, in their work, the oil was represented by just a single triglyceride (and not by its detailed composition). Inaddition, a detailed kinetics were not used. Also, note that using pure oil for biodiesel production is not attractive due to its high cost and limited availability.

Table 2.2a Recent applications of PWC in biodiesel production.

	Process	Highlight(s)	Reference(s)
1	Biodiesel process with phase split and recycle in the reactor system	• Studied the control of biodiesel process with phase segregation and recycle in the reactor system. • A decentralized control structure worked satisfactorily for ±20% production rate change with a settling time of less than 10 h.	Shen et al. (2011)
2	Biodiesel process using pure oil (represented by a single glyceride)	• Systematic IFSH method is adopted. • Single triglyceris is considered that does not provide real industrial scenario where WCO/Crude oil is generally used.	Zhang et al. (2012)
3	Biodiesel production from oil with FFAs (5-50%) using sugar catalyst	• Studied disturbance of ±20% in production rate and ±5% in FFA content.	Cheng et al. (2014)

Cheng et al. (2014) studied the plantwide design and control of a biodiesel process using a sugar catalyst. They tested the developed control structure for the disturbance of ±20% in production rate and ±5% in FFA content in the oil. They found that the transients of the process is slow. According to them, this can be attributed to the large holdup in the reactors that is require to provide the appropriate residence time (of about 2 h). The main advantage of their work is that the catalyst (i.e. sugar catalyst) is less expensive and more environmentally friendly than the conventional catalyst because it does not have to be neutralized and there is no formation of the waste salt. They reported that that total annual cost of the plantwide

process does not change significantly when the FFA content greater than 15 wt%. they have also represented the oil by a single triglyceride (i.e triolein) and single FFA (i.e. oleic acid). Zhang et al. (2012) developed PWC for the biodiesel production from pure vegetable oil, which does not require the esterification section that is required while using WCO as a feedstock to convert the FFA into biodiesel. They used a systematic IFSH methodology for the biodiesel production from pure oil. The control structure developed by them worked satisfactorily for ±10%change in the feed oil. Later, they evaluated the performance of the control structure for some advance criteria, such as settling time, deviation from the production target and dynamic disturbance sensitivity.

All above studies share a common drawback that they have not considered the detailed constituents of the feed oil and realistic kinetics of the esterification and transesterification reactions. Although PWC has been actively studued for many industrial processes, such studies are absent for the homogeneously catalyzed biodiesel production from WCO). So far, only three studies have been reported on the PWC of the complete homoheneously catalyzed biodiesel processes. Also, several PWC studies have also been carried out for real complex industrial processes (namely, toluene hydrodealkylation, Tennessee Eastman processes, HDA process, vinyl acetate monomer process, and styrene monomer plant), PWC of a complete biodiesel process is very limited. A few recent articles on PWC of the biodiesel processes include: biodiesel production using pure vegetable oil. This does not require the pretreatment section, and hence, the control structure is different. Also, most of the previous PWC studies do not check the performance of the developed control structure against advance performance evaluation criteris, such as DPT and

TV. In addition, it can be conluded from the Table 2.2a that IFSH methodology, which is very systematic and finds diverse applications, has not been used for the concerned process in this study. Merits of IFSH methodology are presented below.

2.4.3 Integrated Framework of Simulation and Heuristics (IFSH)

As discussed in the earlier section, modern potential PWC methodologies include IFSH and SOC. Both methodologies are systematic and proven to be successful to yield stable PWC system for many applications. However, the IFSH methodology proposed by Murty Konda et al. (2005) has the unique advantage of using rigorous process simulators in each step of the control structure synthesis and is having lesser computational load. IFSH makes use of the rigorous process simulators to capture dynamic process behavior, and use them to aid in control decision making in addition to heuristics and also to validate the heuristics. The tiered methodology has eight levels, each of which deals with the specific task, based on a hierarchy of priorities. Levels 1 and 2 deal with the important details/requirements such as definition of control objectives, determination of control degrees of freedom (CDOF) and tuning criteria, prior to control structure synthesis. In levels 3 to 5, particular controlled variables are considered at each level corresponding to their significance and implications to the plant. Accordingly, appropriate manipulated variables are chosen.

Level 3 deals with the control decisions relating to product requirements such as throughput and product quality. Chemical process industries are product-centric, and hence it is important to give priority to these controlled variables. Also, the

determination of TPM is important as it may have significant impacts on other loops as they must form a self-consistent structure. Therefore, TPM and product quality manipulator are dealt with in level 3. In level 4, process constraints such as equipment and operational constraints are first considered as controlled variables. These are important to address safety concerns. It is then followed by level and pressure loops. Rationally, it is beneficial to consider level loops before other composition controls and unit operation control loops because levels are often integrating that may lead to instable plant operation. Control of unit operations are then dealt with in level 5. Subsequently, material inventory is analyzed taking into account the effects of integration in levels 6 and 7. Finally in level 8, any further improvement can be considered using the remaining CDOFs, if required. Detailed application of IFSH to current biodiesel production process is described in Chapter 3. Some of the recent applications of IFSH methodology is presented in Table 2.2b.

Murthy Konda et al. (2005) proposed an integrated framework incorporating the simulation and heuristics. They applied this approach to the hydrodealkylation of toluene. They reported that this new approach reaps the advantages of the advance simulators in the control decision making in addition to the heuristics. Later, Murthy Konda et al. (2006b) developed the control structure for the modified hydroalkyalation process using simulation based heuristics approach. They reported that the dynamics of the most economical process alternative are found to be inferior to those of slightly less economical alternatives, which highlights the neccessity of plantwide studies on the interaction of design and control. Vasudevan et al. (2009b) used IFSH and SOC methodology to the styrene monomer plant. They compared that both methods provide satisfactory control structure.

Table 2.2b Recent applications of IFSH in PWC.

	Process	Main feature	Reference(s)
1	Hydrodealkylation of toluene	• Integrated Framework of Simulation and Heuristics is proposed.	Murthy Konda et al. (2005)
2	Hydrodealkylation plant	• Simulation-based heuristic approach was followed.	Murthy Konda et al. (2006b)
3	Styrene Monomer Plant	• Three PWC methodologies, namely heuristics procedure, IFSH, and SOC were applied and compared.	Vasudevan et al. (2009b)
4	Styrene Plant	• IFSH methology is modified and extended to integrated framework of simulation, heuristics and optimization (IFSHO).	Vasudevan and Rangaiah (2011)
5	Biodiesel process using pure oil (represented by a single glyceride)	• Systematic IFSH method was adopted for the biodiesel process for the first time.	Zhang et al. (2012)
6	Autorefrigerated alkylation Process	• IFSHO was found to perform better in terms of TV for the throughput changes.	Tripathi et al. (2013)

However, SOC involves extensive calculations and provides slightly inferior performance in terms of the dynamic disturbance sensitivity. On the other hand, SOC performs better in terms of deviation from the production target. Later, Vasudevan and Rangaiah (2011) proposed modified IFSH method i.e. integrated framework of simulation, heuristics and optimization (IFSHO). They reported that IFSHO provides

better results in terms of better economic performance. Zhang et al. (2012) used IFSH methodology for the biodiesel production from pure oil and successfully tested the performance of the control structure for ± 10 % change in feed oil. Also, Tripathi et al. (2013) developed the control structure for the Autorefrigerated alkylation Process using IFSHO methodology. They reported that the developed control structure works fine for the various disturbances. Next subsection discusses and reviews the OTS for the chemical processes.

2.5 Operator Training Simulator (OTS)

OTS is a computer-based operator training tool that uses a dynamic simulation of the process that imitates the real process. The dynamic simulator is aften integrated with an emulator of the control system. An OTS uses a dynamic simulation of the process to produce the appropriated data to feed an emulation of the plant's control system. Typically, the major components of an OTS are: dynamic simulator, instructor interface, control system integration software, control system emulator and the operator station. Following subsections discuss need, application of OTS in chemical processes, developmental issues, features, simulator softwares and training issues.

2.5.2 Need of Operator Training Simulator

The activities of the operators during the critical situation in the process directly influence the operation of chemical processes. Nazir and Manca (2014) presented and discussed a solution for immersive training of industrial operators

allowing experiencing the multi-faceted scenarios of actual plant operations. Plant Simulator consisted of a process simulator and an accident simulator to simulate normal and emergency scenarios dynamically. Skilled operators are essential for rapid production starts, the highest process performance, lessening environmental impact and reduction of accidental losses in the complex chemical processes. Hence, there is a need for developing an improved methodology to train operators efficiently as their performance has direct influence on the safety, productivity, profitability, stability and controllability of the process (Nazir et al., 2012). According to Yang et al. (2001), in chemical and petrochemical industries without OTS, most operators get their emergency operations training on the job under experienced operators' supervision. This does not impart adequate confidence in inexperienced operators. Earlier, Drozdowicz et al. (1987) noted that training on the job under experienced operators' supervision does not enhance the skills of operators to an adequate level. In addition, even experienced operators may lose their feel for the process, which directly affects team's operational performance. OTS takes care of this gap by combining the theoretical training and hands-on practice. Manenti (2012) stated that a real plant is no place for training, and prior experience based on dynamic simulation may be fundamental to reduce impact/damages of accidents or even to prevent them. Considering this and decreasing computational costs with advent of computational technology, he stated that the detailed dynamic simulation could support what–if analyses and hazard and operability (HAZOP) studies, which will become a key factor for future computer-aided process engineering (CAPE) applications such as virtual reality, operator training simulation, fault detection and automation approaches. Today, chemical process industries face many challenges such as:

- Quick training of operators within safe environment for higher productivity.
- Retention of knowledge as lifetime experience may disappear with the retirement of experienced workforce.
- Grasping advanced control concepts is not easy for new personnel.
- Continuous up-grading of the control software and hardware may increase the difficulty.
- Limited opportunities for training on the plant due to high level of automation.
- Tight project schedules with the challenge of designing and commissioning new and revamped facilities within short duration.
- Varying process conditions, pipeline's slugging problem and changing feed stocks
- Strict regulatory compliance requirements, especially relating to environmental issues.

OTS provides an effective solution to address the above challenges by training the operators for the emergency scenarios, letting the industries to succeed in the global competition. In addition to the theory and academic qualifications real-time training is essential for operators to acquire the required competence. Simulation is often the only cost-effective and safe way to ensure operators' competence in dealing with normal and abnormal situations, contingencies and operations. Using an OTS can be described as experiential learning. Simulation offers repeatability and consistency, which makes it an ideal tool for training operators and setting a standard of operator competence (Dudley et al., 2008).

In complex industries such as chemical, nuclear and aviation industries that have emphasized the importance of safety, identification of key factors that can degrade/enhance safety is one of the main concerns (Park et al., 2004). From the industrial studies of the 170 largest property-damage losses over the last 30 years, 28% of property losses in the hydrocarbon processing industries are due to operational errors or process upsets (see Figure 2.1).

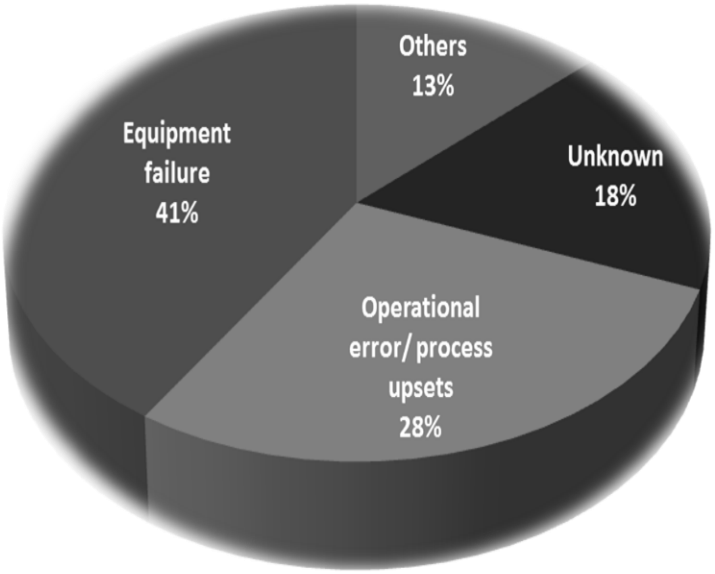

Figure 2.1 Cause and average percentage dollar loss in the hydrocarbon industry (Yang et al. 2001).

According to Fewtrell and Hirst (1974), high-cost accidents share some common features: limited understanding, unfamiliarity with the risks associated with the activities that may lead to accidents in the plant, issues with isolation valves that are not operated remotely, combination of scant and unreliable process control equipment, and loss of process control structure. Glaser (2011) described the need for a systematic approach for implementing OTS to obtain maximum training benefits. He discussed a systematic, five-step approach for implementing OTS over

the long term (viz., identification, normal operation, start up and shut down, troubleshooting, and optimization) along with feedback from OTS users, and use of OTS to develop applied skills (viz., cooperation, communication, supervision and situational awareness). The plant operators receive plant specific and realistic hands-on training ahead of plant start-up and complete plant operation through proper use of OTS. The reliable OTS can also be helpful in other functions such as troubleshooting, developing new operating and control strategies. Thus, the simulator can be a useful tool not only for training but also for the process and control engineers (Dasgupta 1998).

In conclusion, the human error, which is one of the major causes behind the industrial accidents, is the main motivation behind the development of suitable OTS. To increase profitability, companies often extend intervals between plant turnarounds. Therefore, startups and shutdowns occur less frequently. Some emergency situations, such as power supply and steam cutoff, may never occur under normal conditions. Even most experienced operators may perform at high efficiency under these conditions. Using OTS, the trainees can be well prepared for handling such infrequent operations.

2.5.3 Operator Training Simulator in Chemical Processes

High fidelity dynamic process simulators have been widely used by all major oil and gas industries not only within process design studies, detailed engineering studies, process debottlenecking and control system verification but also for operator training (Cameron et al., 2002; Bessiris et al., 2011). In other industries such as palm oil mills, automation is quite limited. Sivasothy and Lim (1985) reported that this

was not due to hardware limitations or reluctance by the industry to adopt automation, but rather due to software limitations.

In the late 1980's and early 1990's, implementation of OTS in the chemical industry has become the common practice. Cameron et al. (2002) reported that training simulators have been widely adopted in industries such as offshore oil & gas industry and power & energy industry, where capital investment is high, processes are complex and the consequences of plant or operator failure are severe. As reported by Cameron et al. (2002), older training laboratories for training in the oil industry were based on physical replicas of the control room which are now expensive and unnecessary.

In industries, object linking and embedding for process control (OPC) is commonly used as industrial communication standard that enables the exchange of data between the server and clients.OPC is a client-server technology that acts as an interface between the server and the client. One application acts as the server providing data while another acts as a client that uses the data. Using OPC standards, applications (e.g. control applications) from different vendors can be linked as they share common standards. Table 2.3 summarizes the applications and main feature(s) of OTS in relevant chemical industries/processes which use modular softwares for the OTS development. However, very limited studies on OTS have been found in the open literature, the number of papers published in this area has increased considerably in the last decade.

Table 2.3 Applications and highlights of OTS in chemical industries.

	System/Industry	Main feature(s)	Software used/ programming	Reference
1	Blending process and distillation process	• Designing and tuning advanced process controllers (APC), for training operator on multi-variable APC, • Pre-configuring connection between the APC controllers and the DCS systems.	SimSuite Pro	Ye et al. (2000)
2	Industrial cracking furnaces in an ethylene plant	• A PC based simulator for industrial cracking furnaces based on the rigorous first principles model which could reflect the effects of the operating variables.	CRACKER, an IBM PC compatible software; Feed characterization module: Neural network	Joo et al. (2000)
3	Batch chemical processes (distillation column and combined subsystem)	• Included a virtual environment similar to a real DCS system.	UNIX environment, C and C++, Solver: gPROMS	Park et al. (2001)
4	Methyl tertiary butyl ether (MTBE) Process	• Incorporated startup, normal operation and shut down.	A set of algebraic and differential equations and neural network	Yang et al. (2001)

Table 2.3 Applications and highlights of OTS in chemical industries (continued).

5	A solvent production plant	• The model is developed with the interfaces emulating the DCS of the real plant.	Hysys	Torres et al. (2004)
6	Ethanol Dehydration (Azeotropic distillation) and debutanizer column	• A virtual environment for industrial process and data representations for operator and engineer training.	Hysys.Plant	Vasconcelos et al. (2005)
7	Bioreactor	• The OTS is developed using the combination of a coding framework and a process control system was found.	eStIM coding framework and WinErs®	Hass et al. (2005)
8	Sugar factory	• Proposed an OTS for a sugar factory, based on the distributed simulation.	EcosimPro	Santos et al. (2008)
9	PETROBRAS' Oil & Gas Production Process	• PETROBRAS' Oil & Gas Production Process and Utilities Simulator Environment called AMBTREI.	Hysys Dynamics	Pereira et al. (2009)
10	Bioethanol fermentation (distillation and biomass power plant)	• User interfaces were designed, on which the user could adjust process control parameters such as for pumps, valves etc., and gain information about relevant state variables.	FORTRAN source code and compiled with the eStIM-software	Kuntzch (2010)

Table 2.3 Applications and highlights of OTS in chemical industries (continued).

11	Petroplus coryton	• OTS included simulations of a heat exchanger and a distillation column.	Simulator by Simulation Solutions, Inc.	Munn et al. (2012)
12	Hydro-dealkylation (HDA)	• Integrated a dynamic process simulator with a dynamic accident simulator for training operators.	UniSim	Manca et al. (2013)
13	Batch processing unit	• Developed OTS is found to be time and cost effective.	UniSim	Balaton et al. (2013)
14	Bioethanol plant	• Studied the influence of process control and automation strategies on the sustainable operation of a bioethanol process.	eStIM for kinetic and sub-unit models implemented in WinErs	Hass (2014)

Ye et al. (2000) developed an OTS for the blending process and distillation column using SimSuite Pro software. The dynamic simulation of the process is carried using SimSuite Pro software that is modular in nature. The OTS included a complete dynamic model of the process and advanced process control system. The OTS was used in operators' training for tuning the advanced process controllers and for pre-configuring the connection between the APC controllers and the DCS systems. An OTS for the industrial cracking furnaces in an ethylene plant is developed by Joo et al (2000). OTS also included a feed characterization module that is built using artificial neural network; This is able to estimate the composition of conventional components from the commercially available indices such as ASTM,

specific gravity etc. An OTS 'CRACKER' developed by them has a user-friendly graphic interface. Park et al. (2001) developed an OTS for batch chemical processes using gPROMS, which they called as 'yOTS'. OTS is built in the INIX environment. Important feature of this OTS was that they included a virtual environent similar to a real DCS system. yOTS is a network-based training simulator, where several trainee can be trained on a single network. The main features of the yOTS include: tutoring the principles of target processes and evaluating the trainee's performance.

Yang et al. (2001) developed an OTS for methyl tertiary butyl ether (MTBE) process. The developed OTS is tested for startup, normal operation and shut down. However, many emergency scenarios, such as utility failure, pump/valve malfunction, etc, are not studied by them. The developed OTS provided valuable experiences on dealing with non-standard operations and in enabling effective start-up policies to be developed. An OTS for the sovent production plant at the Colombian Petroleum Company refinery is developed by Torres et al. (2004) using Hysys. Process model is developed with the interfaces emulating the DCS of the real plant. This enhances the effectivity of the training as emulated DCS is used. They concluded that improved operators' skills, faster plant startups, checking of the DCS configuration, pre-tuning of control loops, modifications design for operation improvements and reduced risk, were obtained.

Vasconcelos et al. (2005) developed an OTS for ethanol dehydration process using Hysys.Plant. They created a virtual environment for industrial process and data representations for operator and engineer training. The virtual environment provided the real feel of the process to make the OTS training more effective. Hass et al.

(2005) developed an OTS for the bioreactor. The model was developed, parameterized and tested using eStIM (a coding framework specialized for the rapid prototyping of dynamic models). WinErs® (process control software) is used for the user interface in the transformation of a standalone process model into an operator training system. Santos et al. (2008) used EcosimPro in the development of an OTS for sugar factory. They described a distributed continuous simulation of an industrial scale case study using DCOM components (DCOM is the Microsoft solution for a component software bus, used by the environments for the creation of distributed simulation).

Pereira et al. (2009) developed an OTS for the PETROBRAS' oil & gas production process and utilities simulator environment called AMBTREI (Training Environment) that imitated the actual control room of an E&P semi-submersible platform at a very high fidelity level. They used Hysys for process model development. However, they have not studied the transients of the process under emergency scenarios, such as pressure relief valve, bursting disks, fire, utility failure etc. Kuntzch (2010) used FORTRAN source code and compiled it with the eStIM-software package for the development of an OTS for Bioethanol fermentation process. The individual models are combined and supplemented by WinErs-control structures to form an overall-process model. Munn et al (2012) used Simulator (by Simulation Solutions, Inc) for the OTS development for Petroplus coryton (heat exchanger and distillation column). The heat exchanger and distillation modules are accompanied by a virtual reality (VR) outside operator view in which the students can locate, monitor, and operate various field devices such hand valves, block valve, pumps, etc. Application of UniSim is also found in the OTS development. Manca et

al. (2013) developed an OTS for the Hydro-dealkylation (HDA) using UniSim sodtware. They presented a training solution based on Virtual Reality (VR) and Augmented Virtual Reality (AVR), specifically addressing the process industry.

Balaton et al. (2013) also used UniSim in the OTS development for a batch processing unit. The different modelling solutions, for example, a mixture of water and ethylene glycol, for the batch reactor vessel and the effect of measuring instrument models were studied. Recently, Hass (2014) developed an OTS for the bioethanol plant. They used eStIM for kinetic and sub-unit models, which are implemented in WinErs process control system. The OTS is based on mechanistic and dynamic process models describing the unit operations and equipment such as valves, pumps, etc.

To conclude, this literature review shows that OTS has found it application in the wide areas of chemical process industry. Also, it is concluded from Table 2.3 that most of the OTS development has utilized the flowsheeting tools, such as hysys, UniSim, EcosimPro, ProSim, SimSuite Pro and D-Spice. This is due to modular structure of these flowsheeting tools that offer the flexibility in the vent of the plant modification or scaleup. Also, these tools have capability of being interlinked with control systems (e.g. DCS) via OPC. However, these published studies do not present the transients of the process under emergency scenarios, such as pressure relief valve, fire, steam failure etc. The industries that have mainly adopted the OTS are: petroleum industry, oil and gas industry, petrochemical industry, and power/energy producing industries. The main reasons behind these industries adopting OTS can be listed as: the high risk in terms of the safety and capital.

On the other hand, the OTS is not commonly used in the field of bioprocess engineering (such as enzymatic processes) possibly because: 1) normally, the operating conditions are moderate in bioprocesses and so the associated risk is relatively lower, and 2) bioprocesses are usually specialized and operated on a small scale, most on bach scale. Consequently, the benefits of using OTS in bioprocess field have not been properly evaluated. Also, it is worth noticing that the OTS has been reported for biodiesel production from WCO. In addition, sectors such as oil mills and other small-scale chemical industries, have not adopted OTS significantly. This could be due to the reasonably lower risk associated with such processes and the higher cost of OTS. Additionally, it can be concluded that Aspen Plus Dynamics and Aspen OTS Framework has not been used for the OTS development for any chemical process. Therefore, there are enough scopes for the exploration of the OTS development. Also, it is important to note that the benefits of process models can be greatly extended by transferring them into an OTS. The issues related to the OTS development and implementation are described in the following section.

2.5.4 Issues Related to the Development and Implementation of Operator Training Simulator (OTS)

Although OTS have been developed and applied in various industries, there are still many challenges related to the OTS development based on steady state design information. According to Yang et al. (2001), a major plant accidents are more than five times more likely to occur during abnormal operations than during normal operation. Qiu et al. (2003) reported that the interest in the study of dynamics

of chemical plants with recycles and plant-wide control design has increased significantly in the past decade.

An acceptable dynamic model requires details of equipment size and shape, controller tuning, sampling time, signal noise, valve hysteresis or shutdown categorizations. The chemical reactors are the key elements in chemical processes. The reactors are often the most complicated unit to model as each reactor has a unique geometry, flow arrangement and reaction kinetics. Consequently, detailed knowledge of the reactor is necessary for developing the realistic reactor model for OTS. As reactors are usually proprietary, their developers are often reluctant to share details about reaction kinetics and reactor design with OTS developers. Under such circumstances, a simplified model or a black box model is used (Cameron et al., 2002).

If the model is highly complex, it will not be easy to modify or maintain online model-based applications (OMBA), and some or all of the value of a complex model may be lost. On the contrary, if the model is too simplistic, there are associated maintenance issues with refitting/retuning and the OMBA value may be lost (Pantelides and Renfro, 2013). However, Pantelides and Renfro (2013) mentioned that sustainability is not always a monotonically decreasing function of the degree of modeling rigor. Infrequent situations like disturbance handling or even system restoration, dictate additional modelling requirements for system performance within the simulator (Spanel et al., 2001). These are discussed in the following sub-sections. Cox et al. (2006) described the salient characteristics of a suitable dynamic modelling tool, as presented in Table 2.4.

Table 2.4 Model Requirements and their Significance (adopted from Cox et al., (2006)).

Model feature (s)	Significance
Dealing with larger processes	• Crucial for plant-wide scenarios • Needed for complex processes
Effective help	• Quick assistance • Rapid action
Efficient solver	• Controlling the model the way a real plant is controlled • Focus on the process and not the solver's quirks
Extensibility	• Model the unusual quirks, special features in the processes
Extensive library of unit operations	• Speed of development • Leverage the best approaches used by experts
Interactive-virtual reality	• Increases user productivity • Reduces modeling errors
OTS	• DCS configuration checkout • Validate operating procedures • Improve operators' skills
Saving states	• Saving states to replay the scenarios
Speed	• Improves productivity
Thermodynamic data	• Appropriate thermodynamic data are needed to develop the model accurately • Often the major obstacle while working on a new model
Visual displays	• Better understanding • Enable immediate feedback on plant performance

A real time dynamic simulator, to be used in OTS, should allow simulation of existing plant as well as the newly introduced processes according to plant demands (Drozdowicz et al., 1987). Therefore, the simulator should be designed in a modular

fashion, where different flow sheets are built combining the unit operation modules in a puzzle like manner and new modules can be introduced with minimal changes. The model equations should be structured carefully as establishing an accurate steady-state solution for the initialization of the dynamic model is very crucial.

i. Model Accuracy

Both the model and modelling tool should be sufficiently accurate to ensure fidelity and consistency of results. Stawarz and Sowerby (1995) used the standard of less than 2% and 10% error for critical and non-critical parameters, respectively, in a model developed for OTS. Considering this, surprisingly simple models can yield sufficient fidelity for operator training needs, they opined. Zhiyun et al. (2003) also stated that, when the ultimate goal of the simulation work is to build OTS, requirements of modeling accuracy are not so strict.

ii. Speed

Cox et al. (2006) stated that if the model can run about 50 times real time, the engineer's effectiveness is highest. Because of an inevitable need for reduced runtime of model while ensuring sufficient fidelity, an appropriate choice of a solver is essential. In addition, flow sheet partitioning can help reducing the model runtime as discussed in Chapter 3. Although the speed up/slow down features provide some flexibity during training, it is more beneficial to use the actual dynamics.

iii. Robustness

The modeler should be able to deal with process issues efficiently without having limitations of issues like convergence, tear streams, solver's incapability, especially, in case of unavailability of good initial guesses. '*In some cases, companies had to delay their projects due to unavailability of good initial guesses*,' Cox et al. (2006) reported. For varieties of disturbances (including shut down of a unit), the model should be able to provide a solution. This is essential, especially when the end user does not have the background to comprehend what is going on in the simulator and thus cannot fix any numerical problem that may arise (Laganier, 1996).

iv. Memory

The model should be able to run for long intervals without overflowing memory or other computer resources. This is a key requirement of an OTS, which runs for hours and days. Cox et al. (2006) reported that commercial dynamic simulators failed at this task. However, our recent experience shows that modern software packages seem to be good in this issue.

In summary, the development of the dynamic simulator for training purpose requires knowledge in several fields: development of the dynamic model of processes, solver, real time programming of digital equipment, programming tools, man-machine interface, etc. Therefore, it is advisable to involve the people having a global understanding of the ultimate goal while each of them having specialized

knowledge of a few of the fields involved development of OTS. In addition, it is essential to maintain the OTS. Otherwise, it may become just a check-off requirement rather than being a learning tool. A poorly maintained OTS may be worse than not having one at all because operators would falsely think that they know what is going to happen, and any such OTS will give the management a false sense of security. Degree of accuracy, calculation speed, convergence and the robustness of a model to be used for operator training need to be given special consideration. Also, it is important that the process model and control system (either emulated or stimulated) should run on a compatible platform in order to provide seemless data transfer and synchronization. Next section presents the salient features of OTS.

2.5.5 Salient Features of Operator Training Simulator (OTS)

A good OTS should posses several features that are essential for extracting the maximum benefit. Usually, dynamic simulations in OTS are considerably detailed containing all equipment items in the plant including items not normally included in an engineering study model (such as instruments and spare pumps). Consequently, these simulations are very large and include operations having fast dynamics and slow dynamics as well, e.g. compressors having fast dynamics and distillation columns having slow dynamics. The integration size must be different catering to the respective dynamics of the unit operations involved to obtain reasonable accuracy. A single processor may lead to simulation time lagging behind real time due to the limited processor capacity. A suitable OTS framework must be able to cope with this by some means. The other features of OTS are as follows;

- Modeling for the entire life cycle of a plant i.e. from the steady-state design to offline engineering studies and on-line operational models (i.e., full-scope operator training for start-up, shutdown and other infrequent operations).
- Modelling equipment failures and logical procedures.
- Sufficient fidelity models to quickly acquaint operators with new controls and human-machine interface (HMI).
- Efficient simultaneous pressure/flow network solvers within fast transients.
- Modeling in the modular fashion so that a new module can be added at minimal cost and effort.
- Ability to evaluate DCS functionality before the start-up of the plant.
- High fidelity models suitable for DCS, safety instrumented systems (SIS) and programmable logic controller (PLC) control validation.
- Object oriented and on-line configurable graphical interface.
- Ability to validate DCS input-output configuration in the most efficient manner possible.
- A framework that provides a configuration mode to set up all the required data links between the dynamic model(s) of process and the other OTS components. Data communication links handle the exchange of data and commands. They should be based on a technology which defines the standard interface for allowing applications to access data from different process control devices such as object linking or embedding (OLE) process control (OPC). Contemporary OPC interfaces considerably reduce the time required to build a good interface to external systems (Cox et al., 2006).
- Software packages (i.e. Emulators) should be able to translate and emulate plant's actual control system into modules that can be used within the OTS

system without the need to buy a replicate control system, thus reducing the OTS cost significantly.

- User Interfaces should support different views of the application for operators, engineers and training instructors. For operators, OTS application should look and behave like the plant's actual control system.
- On-line parameterization/validation of process equipment and control modules.
- Partitioning and configuration of a large dynamic process model across multiple CPUs/cores for faster solution.
- One process flow diagram (PFD) environment to be used to build the model and compact faceplate interface to controllers.
- Profile charts (e.g., column temperature, pressure and composition profile).
- An extensive and useful help system for all OTS users.

To conclude, it is important that the OTS posses several salient features that would make users to extract the maximum benefits from the OTS training. The important factors that must be paid attention to are: detailed dynamic simulation, good user interface, single PFD environment, one model-many uses policy, commom platform (e.g. OPC), and extensive help. Also, it is crucial to consider the specific requirements of the industry while developing the OTS as the training cost is also an important factor. The cost of OTS can be reduced by making use of the components of OTS available with the industry, for example, the emulators as discussed before. Using commercial software packages adds to the convenient development of the OTS. Several commercial software packages available to develop the OTS are described in the next section.

2.5.6 Simulation Softwares for Developing Operator Training Simulator (OTS)

The computer-aided process design (CAPD) and the simulation tools have been successfully implemented in chemical and oil industries since the early 1960s, aiming for the development and optimization of integrated systems (Balaton et al., 2013). The current modular commercial process simulation softwares flexible and convenient model development of the complex processes. A suitable process model and its simulation are at the heart of OTS. However, no model is completely accurate. It is important to note the admonition of Box (1979): 'All models are wrong, but some are useful'. The process dynamic simulators are popular tools for training the operators (Glasscock and Dale, 1994). Previously, the graphical front-ends of large scale operator training simulators consisted of hundreds of thousands of lines of code (Stawarz and Sowerby, 1995).

According to Stawarz and Sowerby, (1995), development of training simulators using procedural code used conventionally will become excessively costly, difficult to update and ultimately unmanageable due to the increased and continuous demand of graphical complexity. To counteract the implications of increasing code length and program complexity, Stawarz and Sowerby (1995) suggested development of graphical interfaces using object-oriented programming methods. Shepherd (1986) reported that it is reasonable to consider training simulation requirements in advance before making a decision to purchase simulation hardware.

Komulainen et al. (2012) reported that use of commercial process simulators in chemical engineering education is an increasing interest. Commercial simulators include Aspen Plus and Aspen HYSYS (Aspen Technology, Inc.), ChemCAD (Chemstations, Inc.), HYSYS (Hyprotech, Ltd./AEA Engineering Software in the past), UniSim Design (Honeywell International Inc.), PRO/II (Simulation Sciences, Inc.) and DYNSIM (Invensys Inc.). Aspen Custom Modeler (ACM), earlier SpeedUp from Imperial College London which was commercialized by Aspen Technologies and named ACM. ACM is used to develop rigorous models of processing equipment.

Aspen Technology, Inc. has provided an Aspen OTS framework in their newer version V7 (and above) that offers a single integrated platform for Process Training and Operator Training Simulators. Shadow Plant™ Standard Edition (Shadow Plant SE) is the dynamic simulator software for the training of operators on Honeywell's regulatory and logic control. Invensys has also been providing OTS for the process industries. Software packages such as DYNSIM and D-splice have also been used successfully by OTS developers such as Hyperion Systems Engineering and Fantoft Process Technologies respectively. Honeywell's UniSim Design software has widespread usage in OTS applications. The first process simulator designed for batch processes called 'Batches' was commercialized in the mid 1980s by Batch Process Technologies (Balaton et al., 2013). The model building strategy in batch processes differs from the conventional method used for continuous processes, for which a steady-state model is first created and then it is switched to dynamic mode. Among all commercial softwares/tools available for the simulation of chemical processes, those commonly used for OTS development are presented in Table 2.5. By no means does this table include all available software packages.

However, an attempt has been made to list some of the most popular commercial flowsheeting softwares having modular structures.

Table 2.5 Commercially available software packages for OTS development.

Software package	**Supplier**
Aspen Dynamics & HYSYS Dynamics (with Aspen OTS framework)	Aspen Technology
ASSETT	Kongsberg Oil & Gas Technologies (KOGT)
AUTODYNAMICS	Trident USA (now owned by RSI)
AZprocede	AZprocede
CC-Dynamics	Chemstations
D-SPICE and K-SPICE	Kongsberg Oil & Gas Technologies
DYNSIM	Invensys (SimSci-Esscor)
INDISS Plus	RSI
JADE	GSE Systems
K-Spice	Kongsberg Oil & Gas Technologies (K-Spice)
OLGA	SPT Group (now acquired by Schlumberger)
OTISS	Honeywell
Petro-SIM	KBC
ProDyn	Ingenious
Shadow Plant	Honeywell
Simcon^{X}	RSI
TSC Sim	TSC Simulation
UniSim	Honeywell
VisSim	Visual Solutions
WSAT	GSE Systems, Inc.

To conclude, it is clear that using the available commercial tools that allow creation of graphical interfaces via object-oriented programming is beneficial for OTS development so long as these tools can imitate the process as real as possible. Using modular simulation software packages, such as UniSim, Hysys, Aspen Plus,

DynSim etc, an effective OTS can be developed. In addition, the promotes the one model-many uses policy that intends to extract the maximum benefits from the process simulations. The use of procedural code to represent the complete plant is tedious and often impractical. The training configurations of OTS and the issues related to them are discussed in the following section.

2.5.7 Training Configurations and Related Issues

'*In defining an approach to deal with the training of process operators, two central issues must be considered - set of responsibilities assigned to a process operator and purpose of training*,' Shepherd (1986) reported. He also stated that, in order to reduce plant downtime and avoid hazards which will affect plant, personnel and the environment, it is important to be clear exactly what sort of skill is required. These skills include detection, diagnosis, compensation, rectification and recovery. Operators are linked with process through a control system, either a DCS or a Supervisory Control and Data Acquisition (SCADA) system where the process controllers are implemented in a number of PLCs (Cameron et al. 2002). Operators need to be trained in how to relate to the process through the DCS or SCADA human-machine interface (HMI). This essentially demands a training simulator to provide the replica of the control system HMI, which can be accomplished in the following ways (Cameron et al., 2002).

- **Stimulated system:** By using the simulator to communicate with a physical copy of the entire control system. Hence, stimulated systems accurately and exactly represent the control system behavior.

- **Quasi-stimulated system:** By using the simulator to communicate with a physical copy of either the DCS operator stations or the SCADA part of a SCADA/PLC control system, and not the entire control system.
- **Emulated system:** By building a software replica of the entire control system and its user interface. However, emulated systems do not ensure the complete fidelity of automation systems and they do not provide accurate implementation of the training system components (Pereira et al., 2009). As reported by Pereira et al. (2009) this system can be preferred when:
    i. Control hardware is difficult to obtain.
    ii. Using physical copy of the entire control system is expensive and worthless, especially when dealing with simpler equipment logics.

Lee et al. (2000) proposed a method of evaluating operators' plant manipulation capability by using an OTS. They developed task evaluation algorithm (TEA) to analyze and evaluate the operators' training results automatically after one finished the training by using the GUI emulation of DCS. TEA includes two main modules: sequence evaluation module (SEM) and quantity evaluation module (QEM). The former indicates whether the operator follows the correct operating sequence that is prepared in advance. On the other hand, QEM gives the deviation of each operator's task from the standard operating procedure. TEA was shown to be efficient and effective in analyzing the operator's capability (Lee et al., 2000).

Several important factors that should be carefully taken into account to perform human reliability analysis (HRA) were observed. Typically, there are three forms of OTS: DCS based, networked workstation/PC and standalone

workstation/PC (Stawarz and Sowerby, 1995). The features and issues related to these training systems are presented in Table 2.6.

Table 2.6 Features and issues related to training systems.

	Training systems	**Features/Issues**	**References**
1	DCS based	i. The control panel is stimulated by an external computer running a dynamic model including controllers.	Shewchuk (1993)
		ii. To co-ordinate the training activity, an instructor is always available to offer assistance, monitor progress and/or add perturbations to the model.	Stawarz and Sowerby (1995)
		iii. In case of a continuous process, a second replica console is required. However, inclusions of the second console can effectively double the cost.	
2	Networked workstations/PCs	i. A central server provides access to the problem database. An instructor can monitor the trainee's progress on-line.	Normand (1993); Shewchuk (1993); Sterky (1993)
		ii. This is mainly suitable when a complex and large scale process is involved (e.g. Petroleum industry),	Stawarz and Sowerby (1995)
		iii. However, Development costs of these types of systems can be high.	
3	Standalone workstation/PC	i. Powerful PCs are required to supply both a high fidelity dynamic model and training front-end.	Stawarz and Sowerby (1995)
		ii. The main features include notably minimal equipment inventory, and hence low inherent costs.	

To summarize, the training system should be chosen based on the facilities available with the industry. The use of the exact DCS environment for training is of notable importance. Decisions, such as use of stimulated or emulated control system, should be done based on the associated cost and the level of training required. To

start with, a standalone OTS can be developed that can then be extended to network base (using real/emulated DCS) training. A solid and up-to-date model with a suitable user interface that mimics the DCS provides much more useful training.

2.6 Summary

A systematic review of previous studies on the biodiesel production, MOO, PWC and OTS is carried out in this chapter. The critical anlaysis of the previous studies identify the gaps in the preious works. These, in essence, set the tone for this research. It is clear from the literature review that homogeneously alkali catalyzed transesterification is the preferred choice in the industry; hence, an OTS should be tested for this process. An effective OTS requires a suitable MOO and PWC study. Consequently, firstly, a detailed literature review has been carried out for the application of MOO and PWC in the biodiesel production. Later, literature review is carried out related to the OTS. Biodiesel production from WCO is attractive due to its many-fold merits, such as low cost and effective waste utilization. Realistic and detailed simulation is important to obtain the close to real results. The reliability of further studies depends mainly on the ability of simulator to yield realistic results. MOO, which is essential given the intense competition among companies and strict environmental regulations, should be made possible using simple, effective and easy to use tools. For example, MS Excel that is popular for several engineering studies due to its familiarity and easy access compared to other more complicated tools. Effective and efficient optimization tool is necessary to obtain trade-offs between several conflicting objectives. Methods such as NSGA-II are proven to be useful in determining such trade-offs in many chemical processes as discussed in Section

2.3.2. Although the production of biodiesel via transesterification has been widely studied, PWC studies and OTS development for this process are absent. The novelty of the present research also includes the development and evaluation of a PWC system for the complex homogeneously catalyzed two-step biodiesel production from WCO. PWC system should be robust and effective. Depending on the objectives PWC structure may vary. Therefore, a systematic procedure should be employed to obtained suitable PWC system. Among several potential PWC methods is an IFSH methodology that has been found to provide suitable control system for variety of chemical processes. Later, the need of an OTS for the biodiesel process is established. Although the accuracy requirements are not so strict, the fidelity of process model is important in OTS development so far as imitating the process behaviour is concerned. Also, it is clear from the review that using the available commercial tools that allow creation of graphical interfaces is beneficial for OTS development so long as these tools can imitate the process as real as possible. Using modular simulation software packages, an effective OTS can be developed. In addition, the promotes the one model-many uses policy that intends to extract the maximum benefits from the process simulations.

Based on the literature review, following gaps in the previous research have been identified: (1) a realistic biodiesel process design and simulation is missing as the previous studies do not use extensive componets of the feed oil and detailed esterification and transesterification kinetics. Stochastic method i.e. NSGA-II has not been employed for the MOO of this process that is required to determine the Pareto-optimal fronts for the conflicting objectives. In addition, scarcity of enough research material on the development of PWC system and OTS development for the biodiesel

production from WCO is clear from the literature review in Sections 2.4 and 2.5. No previous work is found related to the OTS development for biodiesel production from WCO. Additionally, application of APD and Aspen OTS Framework in OTS development has not been explored, thus far. An effective OTS can be beneficial if it is able to yield realistic responses for the range of scenarios. Also, a good OTS should possess several important characteristics of OTS as discussed in this chapter. Next chapter focuses on the methodology adopted to fulfil these gaps that set the objectives of this research.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter deal with design procedures of two alternative processes based on recent literature, MOO, PWC and OTS development for the process. Figure 3.1 shows the flowchart on the general framework of the overall research sequence. Two processes are simulated realistically by using detailed reaction kinetics (10 esterification reactions and 96 transesterification reactions). In addition, detailed constituents of WCO are considered to obtain individual ester content in the biodiesel product. Subsequently, these processes are optimized using Excel based NSGA-II for multiple objectives related to profitability and environment. The two alternate designs are optimized and compared for both economic and environmental interests, using maximum profit, minimum heat duty and minimum organic waste as objectives. Both the process alternatives use alkali-catalyzed transesterification, which is more efficient in terms of faster reaction and better yield. Process 1 is based on the process flow sheet in Sharma and Rangaiah (2013b), where methanol removal is followed by water washing. Process 2 is based on the process flow sheet presented by Morais et al. (2010), where water washing is followed by separation of products. Note that Morais et al. (2010) did not carry out optimization, which is necessary to obtain the maximum benefits. In order to make the two process alternatives comparable, some modifications are made to them, which are presented below. This study considers the sequential approach, where a complete process is simulated in

Aspen Plus and optimized using Excel-based elitist non-dominated sorting genetic algorithm (NSGA-II).

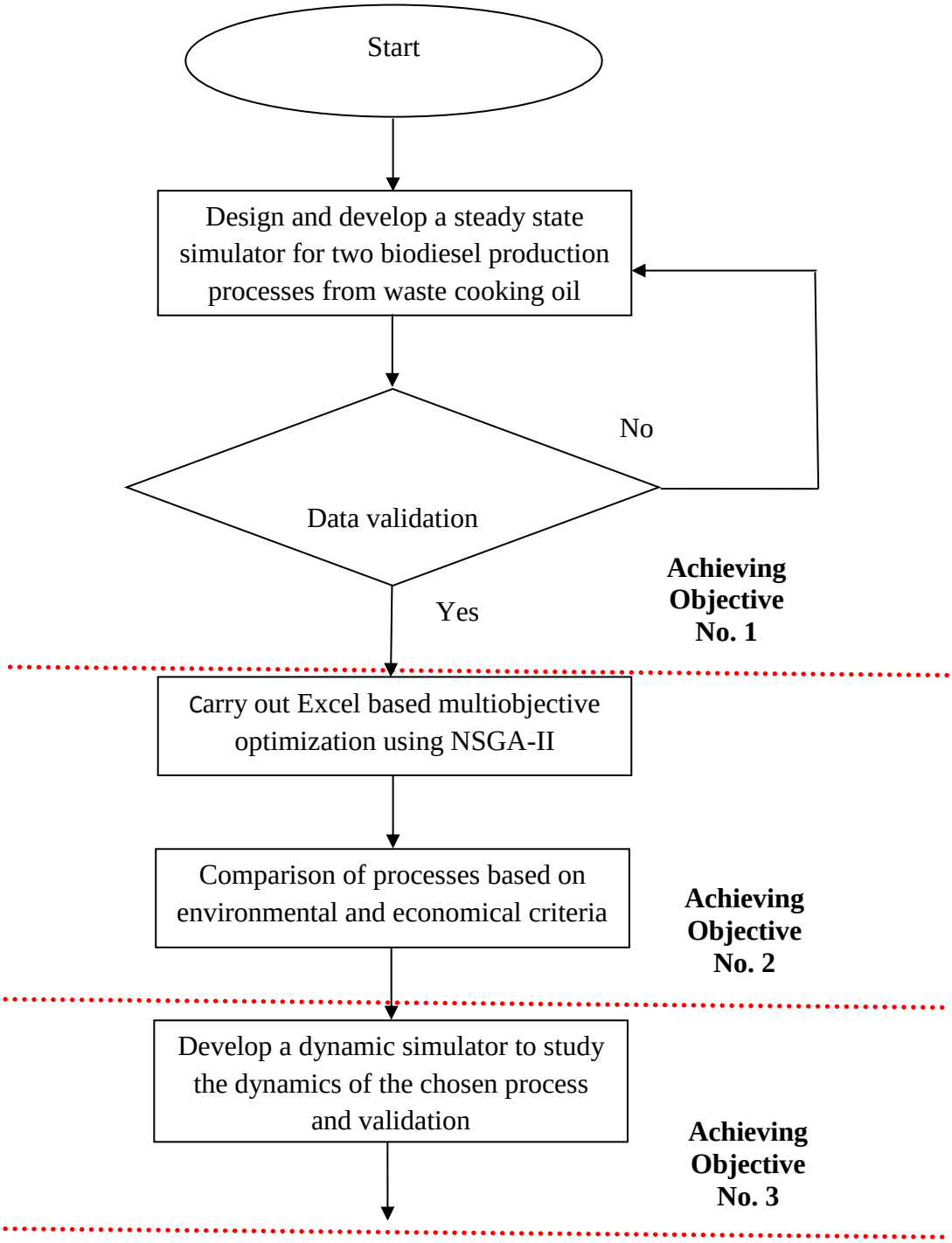

Figure 3.1 Flowchart on the general framework of the overall research sequence.

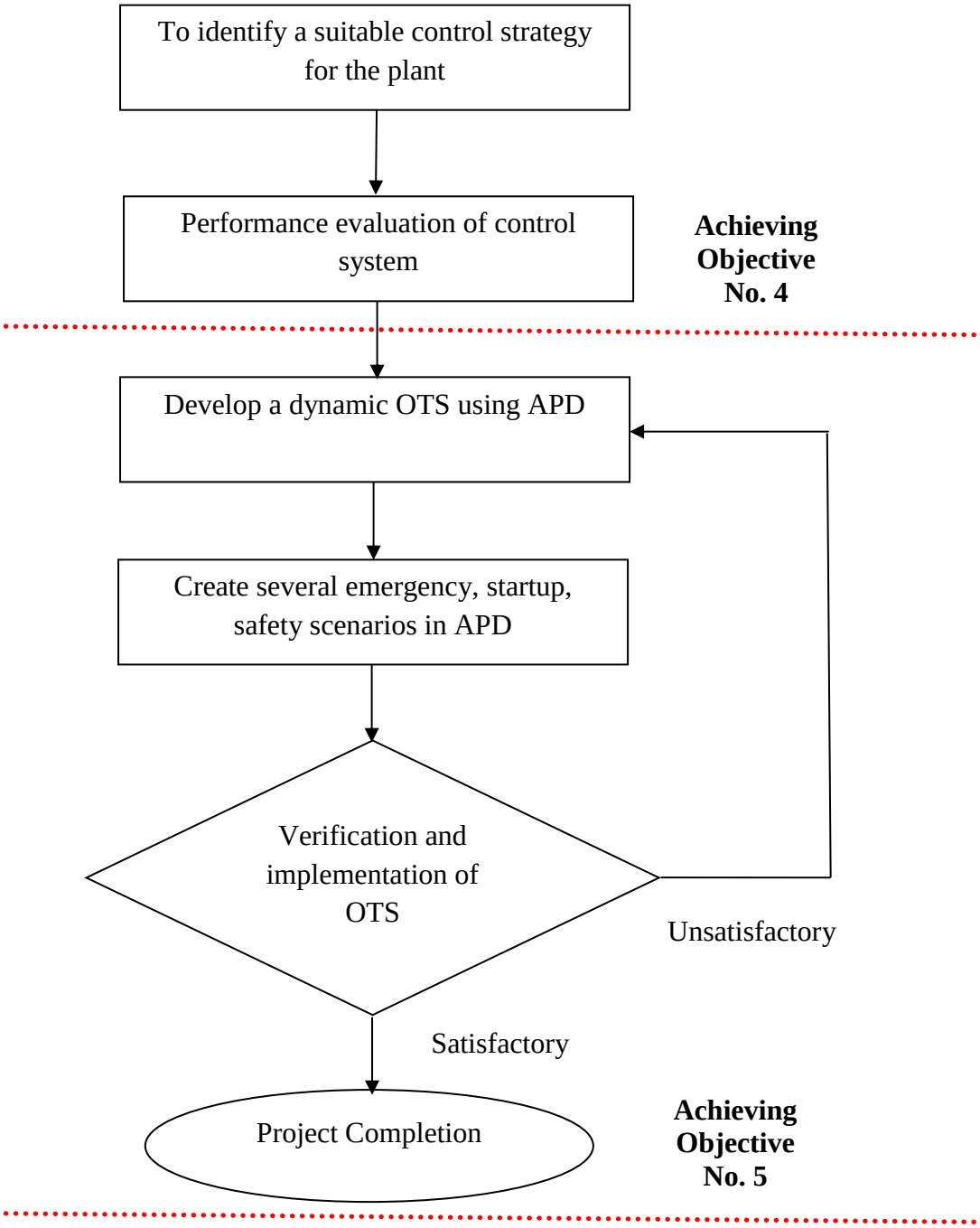

Figure 3.1 Flowchart on the general framework of the overall research sequence (continued).

Costing procedure is also explained based on which the profit is calculated. These processes are then compared based on different criteria for their advantages and disadvantages. Better process is then identified and used for further study on PWC and OTS for biodiesel process. Later, a suitable PWC structure is developed for the chosen process using IFSH method. Optimal paremeters (CSTR temperature, residence time and feed tarys etc.) determined from MOO are used for PWC study. Application of this method is explained in detail in this chapter. Subsequently, OTS development of the concerned process is discussed in detail. For OTS, dynamic model with control structure is developed in APD. Aspen OTS Framework is then used on top of APD. Procedure for scenarios creation is also explained in this chapter. Finally, application of HAZOP to this process is reported.

3.2 Process Development and Process Simulation

In this work, the processes are first simulated in Aspen Plus, and then they are optimized to obtain optimal design and opearation by maximizing the economic potential. This approach is based on the steps proposed by Myint and El-Halwagi (2009). For this study, biodiesel plant capacity is assumed to be 120 kt/annum per annum. This capacity is chosen as the plant with similar capacity already exists. For instance, in Malaysia, a plant is designed to produce 100 kt/annum of biodiesel with infrastructure to expand capacity to 200 kt/annum (PlantBiofuels, 2013). Sharma and Rangaiah (2013b) assumed plant capacity of 20 kt/annum based on the potential WCO availability in Singapore, as estimated by Chua et al. (2010).

Making a similar assumption, in Malaysia, having a population of about six times that of Singapore and having a similar food culture, potential WCO will be around 120 kt/annum. At first, the processes are simulated and compared against the respective reference for the same capacity. Later, the capacity is extended to 120 kt.annum. Plant capacity considered in this study is comparable to this existing plants in Malaysia.

Figure 3.2 presents the methodology followed in this section.

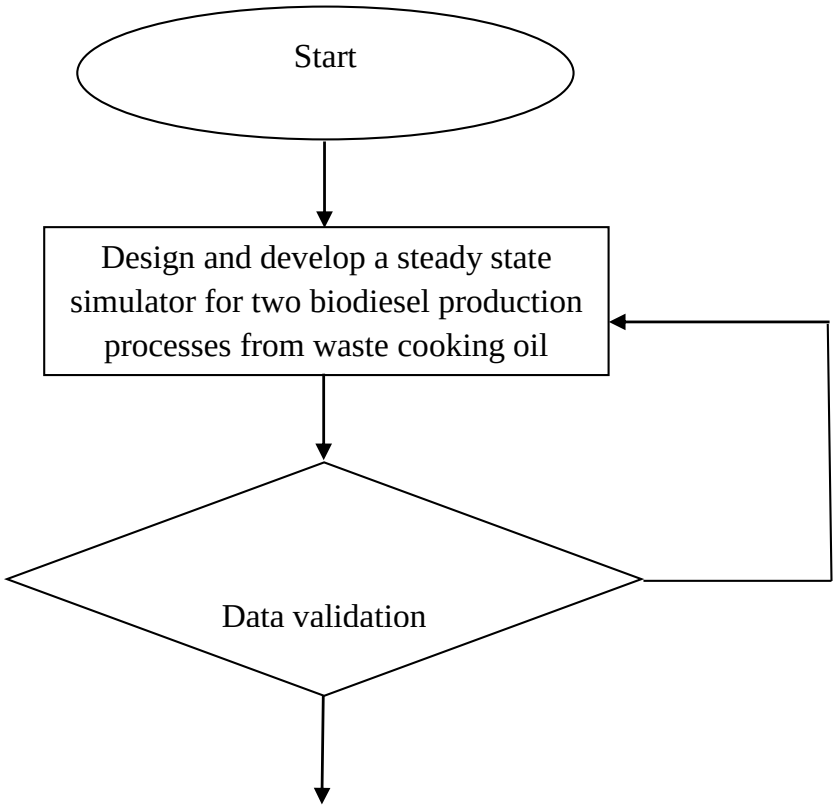

Figure 3.2 Flowchart on the general framework of the process development and simulation.

3.2.1 Process Development

The feed is considered to be waste cooking palm oil (WCPO) as palm oil is extensively used in Malaysia for cooking. However, the processes presented below can process WCO as well as crude palm oil (CPO) as they have similar properties (for example, FFA content: 2-7 %). Note that composition of glycerides may change from even in different WCO collected from different sources. So, actual feed can be either WCO or CPO, depending on their availability and costs.

Two alternative biodiesel production processes are considered and studied to find out the better process. Three reactors are used for transesterification with intermediate phase separators in process 1, whereas just one transesterification reactor is used in process 2. This increases the capital cost due to more reactors, but results into the better production. Also, biodiesel-glycerol separation is followed by methanol separation in process 1. This scheme prevents backward transesterification reactions, as methanol is present until biodiesel and glycerol are separated. Also, the recovered methanol contains a very small amount of water that avoids energy-intensive methanol−water separation and facilitates methanol reuse. Finally, in process 1, washing of biodiesel is carried out at the end that reduces the amount of water required for washing. Both the process alternatives use alkali-catalyzed transesterification, which is more efficient and also used in industrial practice (Lurgi, 2013; Platinumgroup, 2013). Acid pretreatment is carried out to convert the FFA in WCO to biodiesel in both processes. The validation of these processes has been carried out by comparing the simulation results against the data reported in the literature by other researchers, such as Sharma and Rangaiah (2013b), Morais et al.

(2010), Zhang et al. (2012) and Garcia et al. (2010). Initially, the results are validated against the literature data for the capacity considered in the respective source. Then the capacity is increased to the present capacity of 120 kt/annum and compared (see Table 4.1 in Chapter 4). These two biodiesel process alternatives are discussed below.

3.2.1 (a) Biodiesel Process 1

Figure 3.3 shows a process schematic for biodiesel production from WCO, where products separation is followed by water washing (Sharma and Rangaiah, 2013b). WCO with a flow rate of 15,000 kg/h (stream 'OIL' in Figure 3.3) is processed in the esterification reactor (RFFA), where FFAs react with methanol in the presence of acid catalyst to yield FAMEs. The OIL stream is pre-heated in a heat exchanger with the esterification reactor products (stream 'RFFA1'). The esterification is performed at 60^{o}C, 4 bar pressure, methanol (stream 'MEOH') to FFAs molar ratio of 10:1 and with 10% (w/w) of sulfuric acid relative to FFAs (Noureddini and Zhu, 1997). The esterification products (stream 'RFFA1'), after cooling via pre-heating of WCO, are mixed with glycerol and then sent to the phase separator 'W-1', where sulfuric acid and water are separated from the reaction mixture. Glycerol forms two phases with reaction mixture, and acid catalyst is removed in heavy phase. Stream 'W-1-2' containing mainly glycerol, methanol, water and acid catalyst, from the phase separator 'W-1' goes to a distillation column (FRAC-1) where most of the unreacted methanol is recovered and recycled (stream 'FRAC-1-1'). FRAC-1 column has 8 theoretical stages and operates at reflux ratio of 1. The recycled methanol is then fed back to the esterification reactor (RFFA).

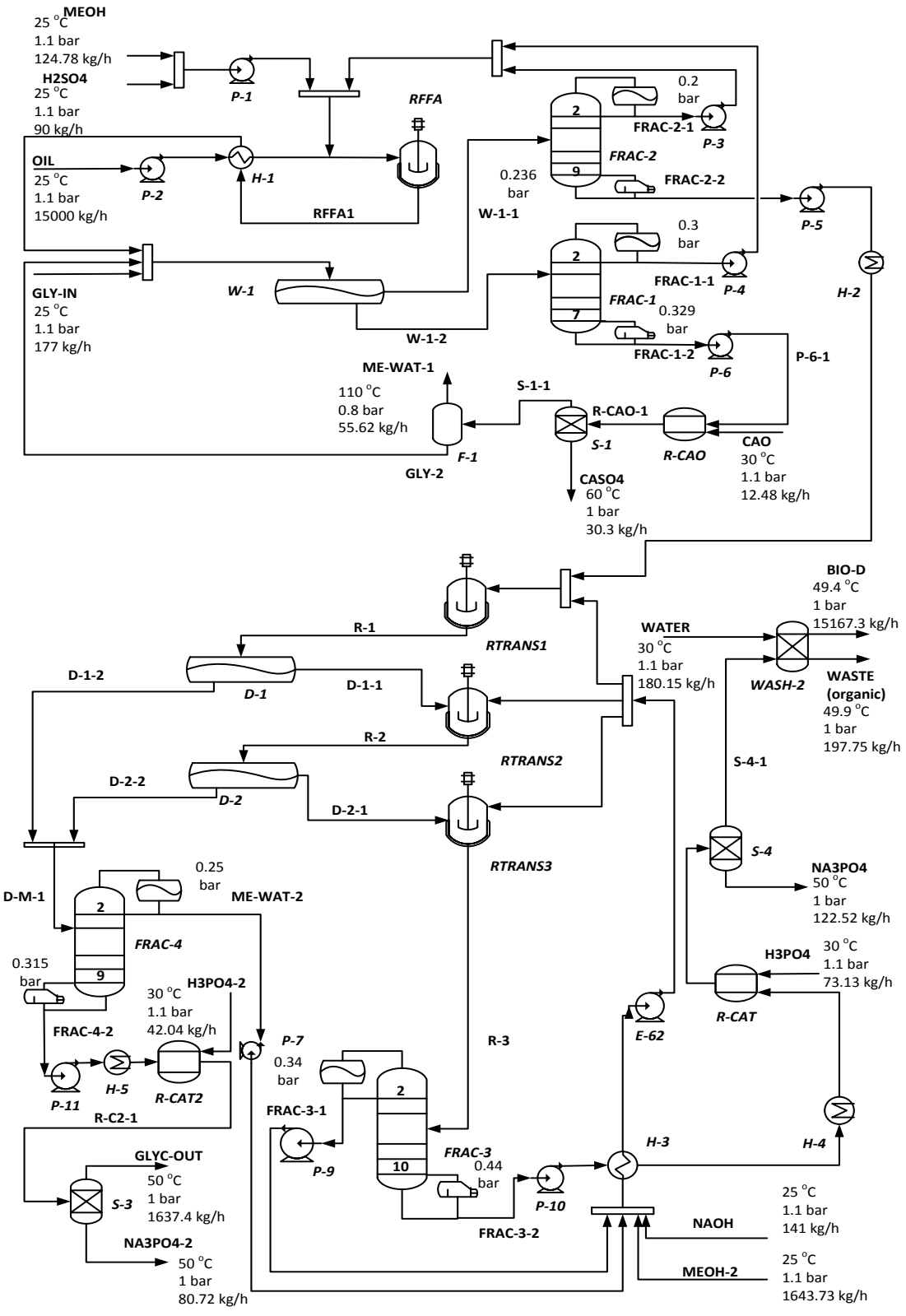

Figure 3.3 Biodiesel production process involving esterification (top section) and transesterification (bottom section): methanol removal is followed by water washing (Process 1).

Glycerol and sulfuric acid leave the FRAC-1 column in the bottom stream (FRAC-1-2), which is then fed to a neutralization reactor (R-CAO), where sulfuric acid reacts with calcium oxide to produce calcium sulphate (stream 'CAO'). The calcium sulphate produced in the reactor is then removed in a gravity separator (S-1). The glycerol stream (S-1-1) leaving the separator S-1 is further purified in a flash evaporator (F-1), where the remaining methanol and water are removed from the top stream (ME-WAT-1) and treated as a waste stream due to small methanol flow rate of 8.53 kg/h. Finally, glycerol is recycled back and mixed with fresh glycerol, which forms two liquid phases in phase separator W-1. The light phase from separator W-1 includes oil, biodiesel, methanol and water while the heavy phase contains glycerol, catalyst, methanol and water. The pretreated WCO feed stream (W-1-1) is fed to a distillation column (FRAC-2 with 10 theoretical stages and operating at reflux ratio of 1), where most of the unreacted methanol (stream 'FRAC-2-1') is recovered in the distillate stream and recycled to the esterification reactor 'RFFA'.

The bottom stream 'FRAC-2-2' containing FAMEs and unreacted oil is processed in the transesterification reactor (RTRANS1 in Figure 3.3) at 50^{o}C. Excess methanol is advantageous as transesterification is a mass-transfer controlled reaction (Noureddini and Zhu, 1997). So, methanol to oil molar flow ratio of 6 is maintained in each transesterification reactor (Morais et al., 2010; Freedman et al., 1984). Transesterification section mainly contains continuous stirred tank reactors (CSTRs), distillation columns, phase separators, a neutralization reactor and a washing column. Three CSTRs are placed in series, and treated oil mixed with methanol and NaOH catalyst is charged to the first CSTR (i.e. RTRANS1). The effluent streams from RTRANS1 and RTRANS2 are individually sent to phase separators, where glycerol

and NaOH with some methanol are separated as the heavy phase (i.e. streams ‘D-1-2’ and ‘D-2-2’). The light phase (i.e. streams ‘D-1-1’ and ‘D-2-1’) from D-1 and D-2 separators goes to RTRANS2 and RTRANS3 reactors, respectively. This phase mainly contains biodiesel, oil and methanol with some NaOH.

Finally, stream ‘R-3’ is charged to a distillation column (FRAC-3) having 11 theoretical stages and operating at reflux ratio of 1, where 98% methanol is recovered and reused in the transesterification reactors. Bottom product from FRAC-3 column contains mainly biodiesel, and is treated in a neutralization unit to remove NaOH using phosphoric acid. A gravity separator ‘S-4’ is then used to separate precipitated salt from stream ‘NA3PO4-2’. It is followed by a water wash column (WASH-2). As the recycled methanol should be free of water, water wash column is used after separating methanol from the reaction mixture. From WASH-2 column, the stream BIO-D containing FAMEs (i.e., Methyl-oleate, Methyl-palmitate, Methyl-myristate, Methyl-stearate, Methyl-linoleate) and having a flow rate of 15167.3 kg/h with more than 99% purity, is taken out.

The remaining unreacted oil, methanol, glycerol, etc. are removed from stream ‘WASTE’ with a flow rate of 197.75 kg/h. Glycerol streams (i.e. streams ‘D-1-2’ and ‘D-2-2’) are mixed together and charged to a distillation column (FRAC-4), where most of the methanol (stream ME-WAT-2) is separated and recycled. The bottom stream (FRAC-4-2) is mainly glycerol and NaOH, and is charged to the neutralization reactor (R-CAT2) to neutralize NaOH present in the streams using phosphoric acid. The Na_3PO_4 formed in the neutralization reactor is separated using the gravity separator (S-3) from stream NA3PO4-2. The top stream ‘GLYC-OUT’,

having more than 96% glycerol, is taken out at a flow rate of 1637.4 kg/h. Figure 3.3 shows temperature, pressure and flow rate of all inlet and exit streams of Process 1.

3.2.1 (b) Biodiesel Process 2

Figure 3.4 shows an alternative process, where washing is followed by products separation, used by Morais et al. (2010). The WCO feed of 15,000 kg/h (stream 'OIL' in Figure 3.4) is pre-heated in a heat exchanger (H-1) with the esterification reactor products (stream 'RFFA1') and then fed to the esterification reactor (RFFA), where FFAs are converted to FAMEs. Esterification takes place at 60^{o}C, 4 bar, methanol (stream 'MEOH') to FFAs molar ratio of 10:1 and with 10% (w/w) of sulfuric acid catalyst relative to FFAs. The esterification products (stream 'RFFA1'), after passing through the heat exchanger 'H-1', are charged with glycerol to the 'WASH-1' column, where sulfuric acid and water are separated from the reaction mixture. Glycerol is added to achieve required separation. Here, a wash column 'WASH-1' is used instead of a phase separator 'W-1' in Process 1. The treated oil that leaves the 'WASH-1' column (stream 'WASH-1-1') is sent to the transesterification reactor. The other stream from 'WASH-1' column (stream 'WASH-1-2') mainly contains glycerol, methanol, water and acid catalyst, which is then sent to a distillation column (FRAC-1 with 6 theoretical stages and operating at a reflux ratio of 1.1) to recover the unreacted methanol (stream 'FRAC-1-1') for recycling to the esterification reactor (RFFA). Glycerol and sulfuric acid leave the FRAC-1 column in the bottom stream (FRAC-1-2), which is fed to a neutralization reactor (R-CAO) where sulfuric acid reacts with calcium oxide to produce calcium sulphate (stream 'CAO').

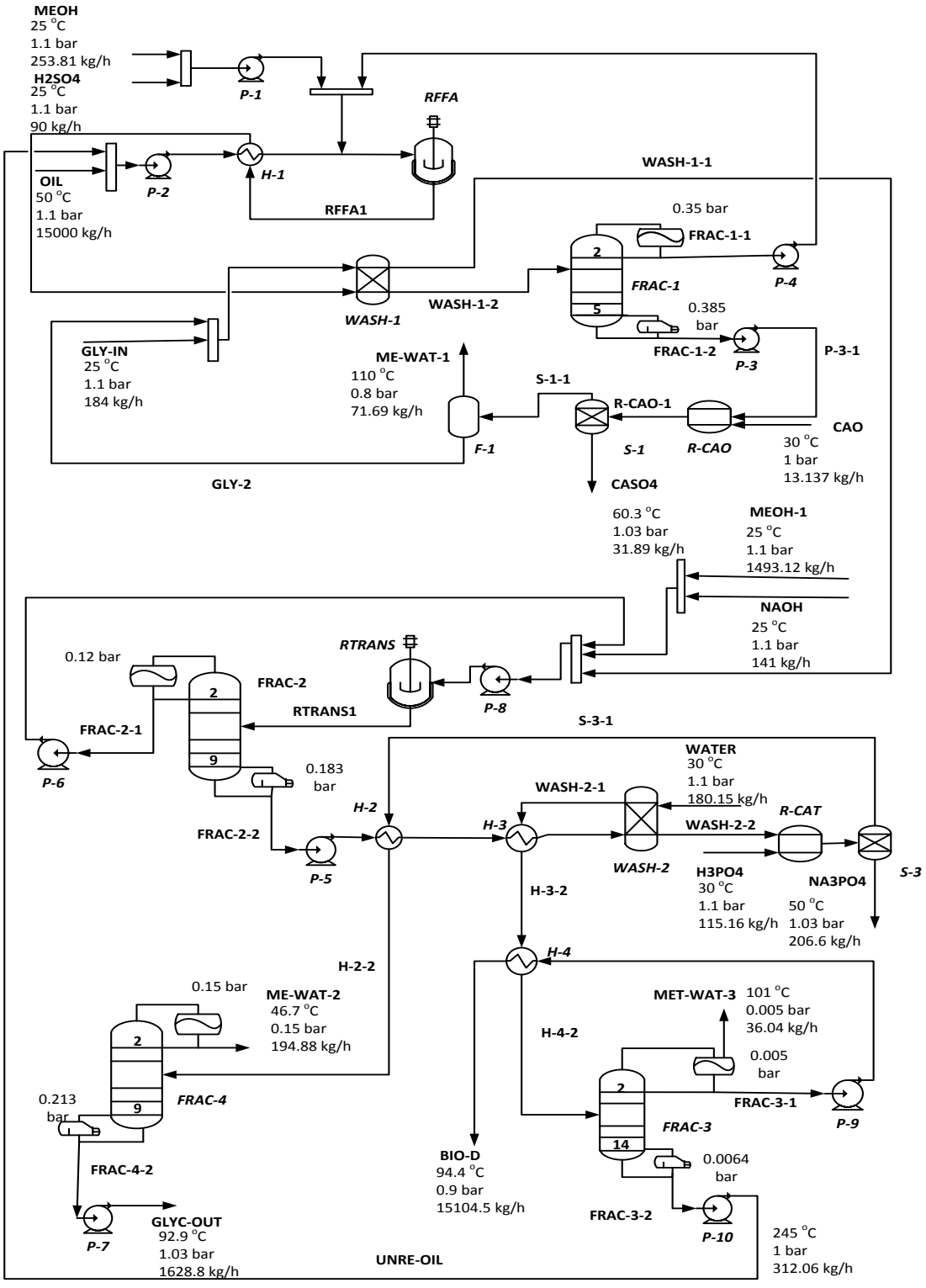

Figure 3.4 Biodiesel production process involving esterification (top section) and transesterification (bottom section): water washing is followed by products separation (Process 2).

The precipitated calcium sulfate is removed in a gravity separator (S-1) and treated as a waste stream (CASO4). The glycerol stream (S-1-1) leaving the separator S-1 is further purified in a flash evaporator (F-1) where the remaining methanol and water are removed in the top stream (ME-WAT-1) and treated as a waste stream due to small methanol flow rate of 14.715 kg/h. Glycerol is then recycled back and mixed with fresh glycerol.

The pretreated oil stream (WASH-1-1 in Figure 3.4) from the esterification reactor is then processed in the transesterification reactor (RTRANS), where a 6:1 molar ratio of methanol to oil is used with 1% (w/w) of NaOH (stream 'NAOH') in oil. Transesterification takes place at 50^{o}C and 4 bar in about 2 h. In addition to the recycled methanol (stream 'FRAC-2-1'), fresh methanol (stream 'MEOH-1') is added to maintain the required ratio of methanol to oil. The anhydrous NaOH is dissolved in fresh methanol. The transesterification products (stream 'RTRANS1') goes to the distillation column (FRAC-2 having 10 theoretical stages and operating at a reflux ratio of 1.0), where 98% methanol is recovered as the column top stream 'FRAC-2-1' and recycled back to the transesterification reactor. The column bottom stream (FRAC-2-2), mainly containing biodiesel and glycerol, flows through heat exchangers H-2 and H-3, where it is cooled using streams S-3-1 and WASH-2-1 respectively; it is then charged to the WASH-2 column. Methanol, glycerol and catalyst are separated from biodiesel and unreacted oil in 'WASH-2'. The stream WASH-2-1, mainly containing biodiesel and unconverted oil, is then fed to the distillation column (FRAC-3) having 15 theoretical stages and operating at the reflux ratio of 1.0. In FRAC-3, a partial condenser is used to separate methanol and water

from stream ME-WAT-3 having a flow rate of 36.04 kg/h, which is not recycled due to its low methanol content (35.6 wt%).

From stream 'FRAC-3-1', biodiesel of more than 99% purity is separated at the rate of 15104.5 kg/h and then used to heat the stream 'H-3-2' in exchanger H-4. Unconverted oil obtained from the bottom stream (FRAC-3-2) at a flow rate of 312.06 kg/h is recycled and mixed with fresh WCO. The bottom stream from the WASH-2 column, containing mainly glycerol (stream WASH-2-2), goes to a neutralization reactor (R-CAT) for removing the catalyst. Phosphoric acid is mixed in equivalent moles to the NaOH present in the stream WASH-2-2. The resulting salt (i.e. Na_3PO_4) is then removed in a gravity separator (S-3). Glycerol resulting from the neutralization reactor (R-CAT) is further purified in a distillation column (FRAC-4) having 10 theoretical stages and operating at a reflux ratio of 1.1. The top stream (ME-WAT-2), containing mainly methanol and water, is not recycled due its small flow rate and methanol content (11.5 wt%). The bottom stream (FRAC-4-2) is more than 96% pure glycerol by-product at a flow rate of 1628.8 kg/h.

Unlike Process 1 (Figure 3.3), a single transesterification reactor is used in Process 2. The effluent of transesterification reactor (RTRANS1) is sent to the distillation column (FRAC-2), where unreacted methanol is separated. As methanol is recycled, reversible reactions might take place; this is undesirable. In addition, bottom product of FRAC-2 is fed to the wash column, and then unreacted oil, methanol and products are separated in FRAC-3 and FRAC-4. Due to this, the recovered methanol contains excess water, which makes it undesirable to reuse. Process 2 uses a distillation column (FRAC-3) with partial condenser to remove

methanol and water in the vapour phase from stream MET-WAT-3. Figure 3.4 shows temperature, pressure and flow rate of all inlet and exit streams of Process 2.

3.2.2 Steady State Process Simulation in Aspen Plus

This section discusses the simulation of the two alternate biodiesel processes. The biodiesel production processes using WCO (shown in Figure 3.3 and 3.4) have been simulated in the Aspen Plus V-8. The palm oil is a mixture of triglycerides of oleic, linoleic, myristic, palmitic, stearic and other acids. Unlike many earlier studies, detailed composition of palm oil is considered in this study. As the detailed composition of waste cooking palm oil is not available in the literature, the detailed composition of refined, bleached and deodorized (RBD) palm oil is taken from Man et al. (1999) and Aspen Technology (2012), and adjusted to include 6 percent FFAs. The detailed fatty acid distribution in diglycerides (DG) is not given. Therefore, all the diglycerides in the feed are represented as the PP molecule (see Appendix A.1). DG such as 1-3-dimyristin, 1-3-dipalmitin, 1-3-diolein and monoglycerides (MG) including 1-monomyristin, 1-monopalmitin, 1-monostearin, 1-monoolein and 1-monolinolein are the intermediates of the transesterification reaction. Methyl-Oleate, Methyl-Palmitate, Methyl-Myristate, Methyl-Stearate and Methyl-Linoleate are the biodiesel products. Table A.1 in the Appendix A lists the detailed glyceride and FFA compositions in the WCO feed.

NaOH is used as the catalyst, and is removed by adding H_3PO_4 to precipitate Na_3PO_4. As the electrolyte chemistry is not modeled in detail, these electrolytes are

simulated using physical property data for water, but considering their correct molecular weights (Aspen Technology, 2012).

In this study, detailed kinetics including intermediate mono- and di-glycerides formation, are considered for obtaining realistic results. Physical properties of mono-, di- and tri-glycerides are taken from the Aspen Plus database. Esterification and transesterification kinetics used are respectively taken from Berrios et al. (2007) and Aspen Technology (2012). The transesterification kinetics in Aspen Technology (2012) are extracted from Narvaez et al. (2007), who reported them for palm oil and not for the individual triglycerides present. Therefore, reaction kinetics of all the constituent triglycerides were assumed to be the same as that for the triglyceride mixture in palm oil. For example, both reactions 1 and 7 (see reaction set A.2 in Appendix A.1) produce DG from triglycerides (TG), and hence their rate constants are considered as equal (Aspen Technology, 2012). Note that the uncertainty in the kinetics may have some effect on the calculations, but this effect will not influence the results significantly. For reliable biodiesel process modeling, it is crucial to capture the non-ideal phase equilibrium as the biodiesel process involves highly non-ideal components.

Shen et al. (2011) used UNIFAC model for the calculation of vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) envelopes in the transesterification system. They reported that the binary azeotrope of glycerol-methanol and the LLE envelope predicted by the UNIFAC model are in agreement with the experimental data. The property model used for biodiesel process simulation is Dortmund modified UNIFAC as researchers (Kiss et al., 2012; Aspen Technology,

2012; Kiss, 2009) successfully used this model to predict the physical properties of the considered components. Redlich-Kwong-Soave equation of state (RKS EOS) is used to predict the physical properties of the vapor phase. Thermophysical property model parameters of tri-, di-, and mono-glycerides such as vapour pressure, heat of vaporization, heat of formation, heat capacity, liquid molar volume and liquid viscosity are taken from biodiesel databank of Aspen Plus. The detailed information for the development of these thermophysical property models has been presented in Zong et al. (2010a), Zong et al. (2010b) and Zong et al. (2010c). In addition, the required T_C, P_C and ω (critical temperature, critical pressure and acentric factor) for RKS EOS are estimated with the Gani group contribution method (Aspen Technology, 2012). A group contribution method is a technique to estimate and predict thermodynamic and other properties from molecular structures. A group contribution method is used to predict properties of pure components and mixtures by using group or atom properties. This reduces the number of required data significantly. A group contribution method uses the principle that some simple aspects of the structures of chemical components are always the same in many different molecules. This method uses the pure additive group contributions to correlate the required property with an easy accessible property such as critical temperature. Although the experimental or industrial validation could not be carried, the simulated results such as conversion in esterification and transesterification section, and product quality have been found in agreement with the literature data (Sharma and Rangaiah, 2013b; Garcia et al., 2010).

A fixed pressure of 4 bar is assumed in both esterification and transesterification reactors while reactor temperatures are considered as decision

variables in the optimization. In both the process alternatives, product purities were defined to be 99% (w/w) for biodiesel, which is higher than the European biodiesel standard (EN 14214) specification for esters content (i.e., 96.5% w/w). Vacuum operation for methanol recovery and products purification is employed for maintaining the temperatures at suitably low levels to avoid the thermal decomposition of biodiesel (< 523.15 K) and glycerol (< 423.15 K) (Morais et al., 2010). Further, atmospheric pressure is assumed in neutralization reactors and water wash columns.

3.3 Multi-objective Optimization of Biodiesel Processes

MOO is carried out for the biodiesel processes to find the optimal parameters. Both biodiesel processes were optimized for profit, heat duty and organic waste. Figure 3.5 presents the flowchart showing the methodology followed in this section.

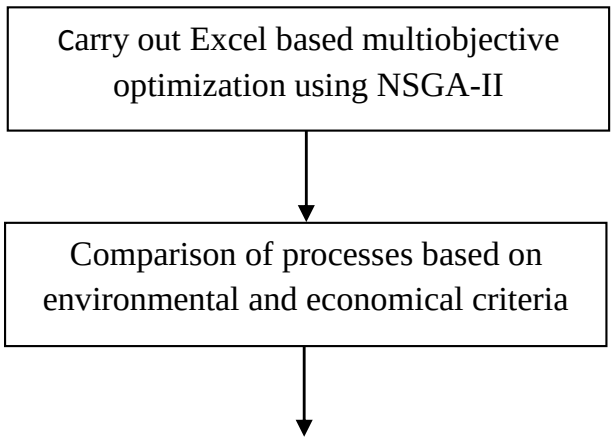

Figure 3.5 Flowchart on the general framework of the MOO.

Methanol, glycerol, tri/di/mono-glycerides, FAMEs and FFAs in stream 'WASTE' and methanol in stream 'ME-WAT-1' in Figure 3.3, are considered as the constituents of organic waste in Process 1. Methanol in streams 'ME-WAT-1', 'ME-WAT-2', and 'ME-WAT-3' in Figure 3.4, is considered as organic waste in Process 2. Profit is calculated by subtracting cost of manufacture (COM) from the revenue obtained by selling the products: biodiesel and glycerol.

Table 3.1 presents the cost of raw materials, products and utilities, used in the present study. As described in Section 3.2, potential WCO is 120 kt/annum (equivalent to 15000 kg/h). Given the uncertainty in the WCO availability, this work considers -20% variation in WCO as one of the decision variables. Temperature and residence time of each of the CSTRs are also taken as decision variables for optimization as these are important for the conversion of WCO to biodiesel. Also, feed stage of all distillation columns is taken as a decision variable as it can minimize energy requirement by reducing reboiler duty. Operating rages are taken based on the previous studies i.e. Sharma and Rangaiah (2013b) and Narvaez et al. (2007). Also, constraints are decided based on the quality requirements and the maximum allowable temperature related to the product deterioration temperature.

In this study, product purities are treated as constraints as these have to be satisfied as per standards. To prevent product deterioration, upper limits for temperatures at the bottom of all distillation columns is considered as additional constraints (Sharma and Rangaiah, 2013b).

Table 3.1 Prices of raw materials, products and utilities.

Raw materials, products & utilities	**Price**	**Unit**	**Source**
Biodiesel	0.9459	USD/kg	Platts (2013)
Oil	0.39	USD/kg	Sharma and Rangaiah (2013b)
Methanol	0.28	USD/kg	Sharma and Rangaiah (2013b)
Glycerol	1.1	USD/kg	Sharma and Rangaiah (2013b)
Sodium hydroxide	0.75	USD/kg	Sharma and Rangaiah (2013b)
Sulfuric acid	0.071	USD/kg	Sharma and Rangaiah (2013b)
Calcium oxide	0.046 (0.07 using CEPCI of 600 for 2013)	USD/kg	You et al. (2007)
Phosphoric acid	0.391 (0.595 using CEPCI of 600)	USD/kg	
Cooling water	2.12×10^{-07}	USD/kJ	Aspen Plus database
Refrigerant (-25^{o}C)	2.74×10^{-06}	USD/kJ	
Low pressure steam (125^{o}C)	1.9×10^{-06}	USD/kJ	
Medium pressure steam (175^{o}C)	2.2×10^{-06}	USD/kJ	
High pressure steam (250^{o}C)	2.5×10^{-06}	USD/kJ	
Electricity	0.0775	USD/kWh	

MOO for both processes is carried out for two different cases: (1) profit and heat duty, and (2) profit and organic waste. Profit vs organic waste is essential as industries look for maximum profit. But environmental regulations may limit it if there is a conflicting trade-off between profit and organic waste. Also, heat duty is related to the environment, and also affects the cost of production. Table 3.2 provides details on these cases considered in this study.

Table 3.2 Different optimization cases for biodiesel production processes.

Objective function	**Decision variables**	**Constraints**
Processes 1 and 2 **Case A:** *Max.* Profit (million USD/annum) *Min.* Heat Duty (MW) **Case B:** *Max.* Profit (million USD/annum) *Min.* Organic Waste (tons/annum)	**Process 1** $96 \leq \text{WCO} \leq 120$ kt/annum $55 \leq T_{RFFA} \leq 65^{o}C$ $45 \leq T_{RTRANS1} \leq 60^{o}C$ $45 \leq T_{RTRANS2} \leq 60^{o}C$ $45 \leq T_{RTRANS3} \leq 60^{o}C$ $1.5 \leq (\text{Residence Time})_{RFFA} \leq 2.5$ h $1.5 \leq (\text{Residence Time})_{RTRANS1} \leq 2.5$ h $1.5 \leq (\text{Residence Time})_{RTRANS2} \leq 2.5$ h $1.5 \leq (\text{Residence Time})_{RTRANS3} \leq 2.5$ h $2 \leq (\text{Feed Stage})_{FRAC-1} \leq 7$ $2 \leq (\text{Feed Stage})_{FRAC-2} \leq 9$ $2 \leq (\text{Feed Stage})_{FRAC-3} \leq 10$ $2 \leq (\text{Feed Stage})_{FRAC-4} \leq 9$ **Process 2** $96 \leq \text{WCO} \leq 120$ kt/annum $50 \leq T_{RFFA} \leq 65^{o}C$ $45 \leq T_{RTRANS} \leq 60^{o}C$ $1.5 \leq (\text{Residence Time})_{RFFA} \leq 2.5$ h $1.5 \leq (\text{Residence Time})_{RTRANS1} \leq 2.5$ h $2 \leq (\text{Feed Stage})_{FRAC-1} \leq 5$ $2 \leq (\text{Feed Stage})_{FRAC-2} \leq 9$ $2 \leq (\text{Feed Stage})_{FRAC-3} \leq 14$ $2 \leq (\text{Feed Stage})_{FRAC-4} \leq 10$	**Process 1** Mass purity: $x_{Biodiesel} \geq 0.99$ Mass purity: $x_{Glycerol} \geq 0.95$ $(\text{Methanol Recovery})_{FRAC-1, FRAC-3, FRAC-3, FRAC-4} \geq 0.98$ $T_{FRAC-1} \leq 150^{o}C$ $T_{FRAC-2} \leq 250^{o}C$ $T_{FRAC-3} \leq 250^{o}C$ $T_{FRAC-4} \leq 150^{o}C$ **Process 2** Mass purity: $x_{Biodiesel} \geq 0.99$ Mass purity: $x_{Glycerol} \geq 0.95$ $(\text{Methanol Recovery})_{FRAC-1, FRAC-3, FRAC-3, FRAC-4} \geq 0.98$ $T_{FRAC-1} \leq 150^{o}C$ $T_{FRAC-2} \leq 150^{o}C$ $T_{FRAC-3} \leq 250^{o}C$ $T_{FRAC-4} \leq 150^{o}C$

Equipment purchase cost (C_p) and bare module factor (F_{BM}) are calculated based on the correlations and data given in Seider et al. (2010). For example, Eq. 3.2 gives the purchase equipment cost of the fixed head shell and tube heat exchanger (HE). Cost equations for all other unit operations have not been shown for brevity. Total module cost (C_{TM}) and gross roots cost (C_{GR}), which is considered as fixed capital investment (FCI), are calculated using Eqs. 3.6 and 3.7, respectively. If the distillation column diameter is less than 0.9 m, then the column is considered to be a packed column; otherwise, trays are assumed in the column (Sharma and Rangaiah, 2013b). All equipments processing acids are assumed to be built of stainless steel, while all other equipments are assumed to be made of carbon steel. Bare module cost (C_{BM}) is calculated using Eq. 3.5. Bare module cost at base conditions (C^0_{BM}) denotes the cost when pressure is ambient and carbon steel is the material of construction.

$$C_B = exp^{\{11.0545-0.9228[\ln(A)]+0.09861[\ln(A)]^2\}} \tag{3.1}$$

$$C_P = C_B F_P F_M F_L \tag{3.2}$$

$$\text{where, } F_M = a + b\left(\frac{A}{100}\right) \tag{3.3}$$

$$F_P = 0.9803 + 0.018\left(\frac{P}{100}\right) + 0.0017\left(\frac{P}{100}\right)^2 \tag{3.4}$$

$$C_{BM} = \sum_{all\ equipments} C_p F_{BM} \tag{3.5}$$

$$C_{TM} = 1.18 C_{BM} \quad (3.6)$$

$$FCI \text{ or } C_{GR} = C_{TM} + 0.50 \sum_{all\ equipments} C^0{}_{BM} \quad (3.7)$$

Where, A is the area of HE, a and b are the constant that are the function of area, F_L depend on the length of tubes and P is the operating pressure. The operating labor cost is calculated based on the procedure given in Turton et al. (2009). Cost of manufacturing (COM) and then profit are calculated using the Eqs. 3.8 and 3.9 (Turton et al., 2009). COM includes direct manufacturing cost (i.e. the cost vary with the production rate, e.g. raw material, utility cost etc.), fixed manufacturing cost (i.e. does not vary with production rate, e.g. taxes, insurance, depreciation etc.) and general expenses (e.g. overhead burden such as management, sales, research, financing etc). Adding these individual costs, COM without depreciation is defined as the following equation. Eqs. 3.10 and 3.11 give the heat duty and organic waste in the process.

$$COM = 0.28\,(FCI) + 2.73\,(operating\ labor\ cost) + 1.23\,(cost\ of\ utilities + cost\ of\ raw\ material) \quad (3.8)$$

$$Profit = Revenue - COM \quad (3.9)$$

$$Heat\ duty = \sum_{all\ equiments} Heat\ duty \quad (3.10)$$

$$Organic\ waste = \sum_{in\ all\ exit\ streams} composition\ of\ methanol, glycerol, unconverted\ oil\ and\ FAME \quad (3.11)$$

In this study, an EMOO program (Sharma et al., 2012), which is based on the binary-coded NSGA-II, has been used for determining the optimal trade-offs between different objectives. In this program, objective functions and constraints are computed in Excel worksheets, whereas NSGA-II is executed inside the Excel Macro (Visual Basic for Applications). Binary coding is employed for implementing the NSGA-II algorithm in the EMOO program by Sharma et al (2012). In the EMOO program, binary tournament selection for participation in cross-over and mutation operations, cross-over by single point, two-point and uniform schemes, and bit-wise mutation are available. The following criteria are used in determining the domination;

i. When the two individuals A and B are feasible, then the definition of domination based on objective values (in step 4 in the above algorithm) applies.
ii. When only one individual is feasible, then the feasible individual dominates the infeasible individual.
iii. When both individuals are infeasible, then the individual with smaller violation of constraint dominates the other individual.

Values of NSGA-II parameters used for all optimization cases in this work are: population size (NP) = 100, two-point crossover with probability = 0.9, mutation probability = 0.05, random seed = 0.5, and maximum number of generations = 100. Two-point crossover, bit-wise mutation and tournament selection for participation in crossover are adopted. The algorithm used in the EMOO program is given below (Sharma et al., 2012);

i. Generate the initial population of NP individuals within the bounds of the decision variables, using uniformly distributed random numbers. The population size 'NP' is a parameter whose value has to be entered by the user. Evaluate the objective functions and constraints of each individual in the population.

ii. New set of NP individuals are generated by selection, cross-over and mutation operations of genetic algorithms over the initial population.

iii. Combine the current population with all the new individuals yielding the combined population of 2NP individuals.

iv. Determine Ndom i.e. the number of individuals dominating each individual in the combined population. Solution A is considered to be dominating solution B, if value of each objective function of solution A is as desirable as that of solution B and at least one objective value of solution A is better than that of solution B.

v. Assign Rank to the individuals. Individuals with the smallest Ndom are assigned a Rank of 1 (the best Pareto front). Individuals with the next smallest Ndom are assigned a rank of 2 (subsequent Pareto front). This continues for all individuals.

vi. Sort the individuals according to their rank, and then calculate the Rank at the NPth individual. This Rank is represented as the NdomCut.

vii. For individuals having Rank equal to NdomCut, find the crowding distance of each individual in the objective space.

viii. Sort the individuals in the combined 2NP population according to the increasing rank followed by the decreasing crowding distance.

ix. The first NP (i.e. the best individuals having smaller rank) individuals in the sorted list from the previous step will form the current population in the next generation.

Repeat steps ii–ix for the maximum number of generations, as entered by the user.

EMOO program is then interfaced with Aspen Plus using visual basic application (VBA) (Figure 3.6). MS Excel takes the required variables (e.g. biodiesel flowrate) from Aspen Plus simulation to calculate objective function (Eq 3.5) and constraint (e.g. maximum temperature in distillation column FRAC-3).

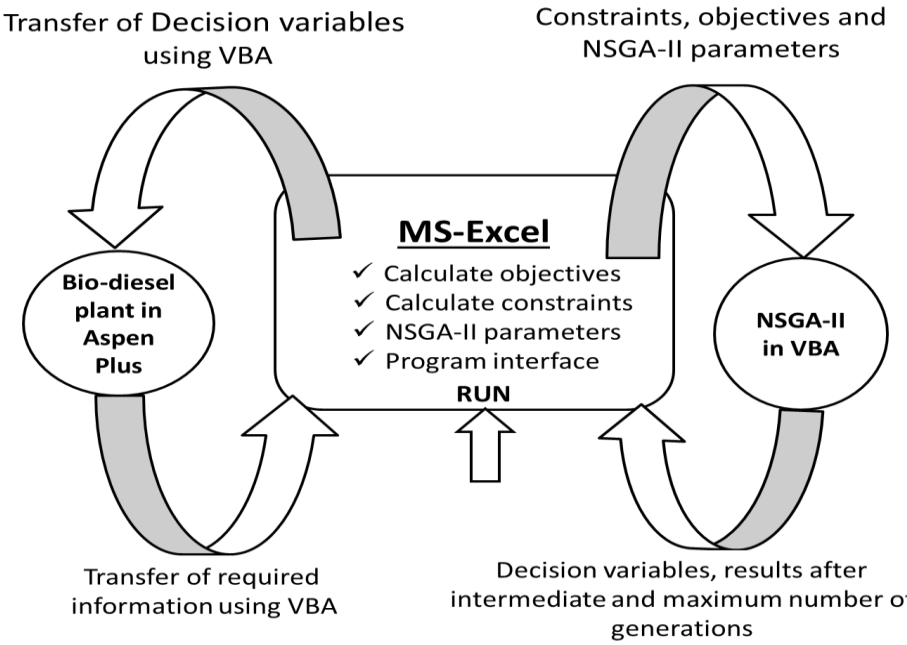

Figure 3.6 Framework for EMOO.

NSGA-II parameters (e.g. number of generation) are provided in Excel, which then go to the VBA for NSGA-II algorithm. NSGA-II in this program generates a set of decision variable values (e.g. temperature in CSTR 'RFFA') (see Table 3.2), and these values are sent to the Aspen Plus simulation via MS Excel. The

simulation is converged for each set of values of decision variables, and required results from Aspen Plus simulation (such as flow rates, mass fractions and utilities) are sent to the EMOO program. In Excel, these results are used to determine the values of objective functions and constraints, which are in turn used by NSGA-II. Then, NSGA-II generates another set of values for decision variables, and the above procedure is repeated. The iterative calculations continue until the specified stopping criterion is satisfied (i.e. maximum number of generation). Later, a dynamic simulation is carried out using APD V8.0. Next section describes the PWC study for the biodiesel process 1.

3.4 Plantwide control of Biodiesel Process 1 and its Performance Evaluation

Figure 3.7 shows the methodology followed in thi section. The process model used in the previous sections is used for this study. The optimal parameters determined in the previous section are used.

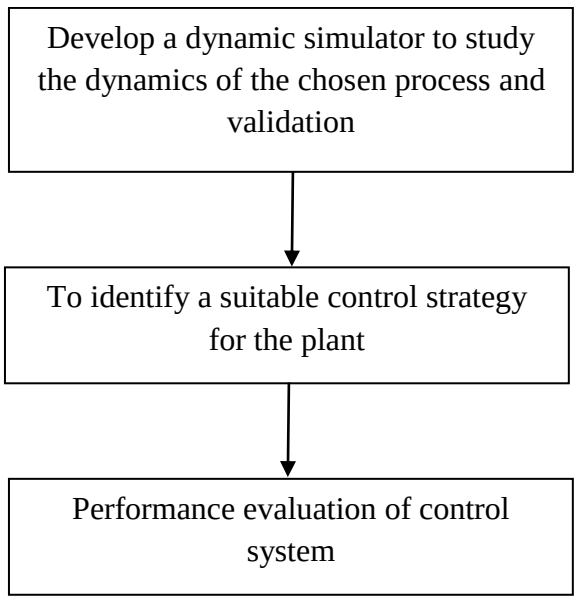

Figure 3.7 Flowchart on the general framework of the PWC.

A PWC system is designed based on IFSH methodology proposed by Murthy Konda et al. (2005). This systematic and hierarchical methodology has eight levels, where, in addition to heuristics, both steady state and dynamic process models are effectively utilized in decision making while designing a control system. For example, decisions based on heuristics are corroborated using dynamic simulations. The main advantage of IFSH methodology is that it overcomes the over-reliance on heuristics to design a decentralized regulatory control system.

In this research, a sequential approach is followed where a better process design is first identified and a suitable control structure is developed for the identified process. Each level of IFSH and its application to the chosen biodiesel (Figure 3.8) process are described below. Figure 3.8 shows the important design and operating parameters. A dynamic simulation model of the process 1 is developed using Aspen Plus Dynamics (APD) V8.0. Distillation columns are operated under vacuum and use cooling water in the condensers. Running distillation columns under vacuum can impact the control strategies significantly as the pressure on the trays can change, affecting tray temperatures.

Surge capacities in reactors, reflux drums and column bases are sized to provide 5 min of holdup when at 50% level. The steady state conditions in the dynamic simulation using APD have been found to be consistent with those in steady state simulation using Aspen Plus.

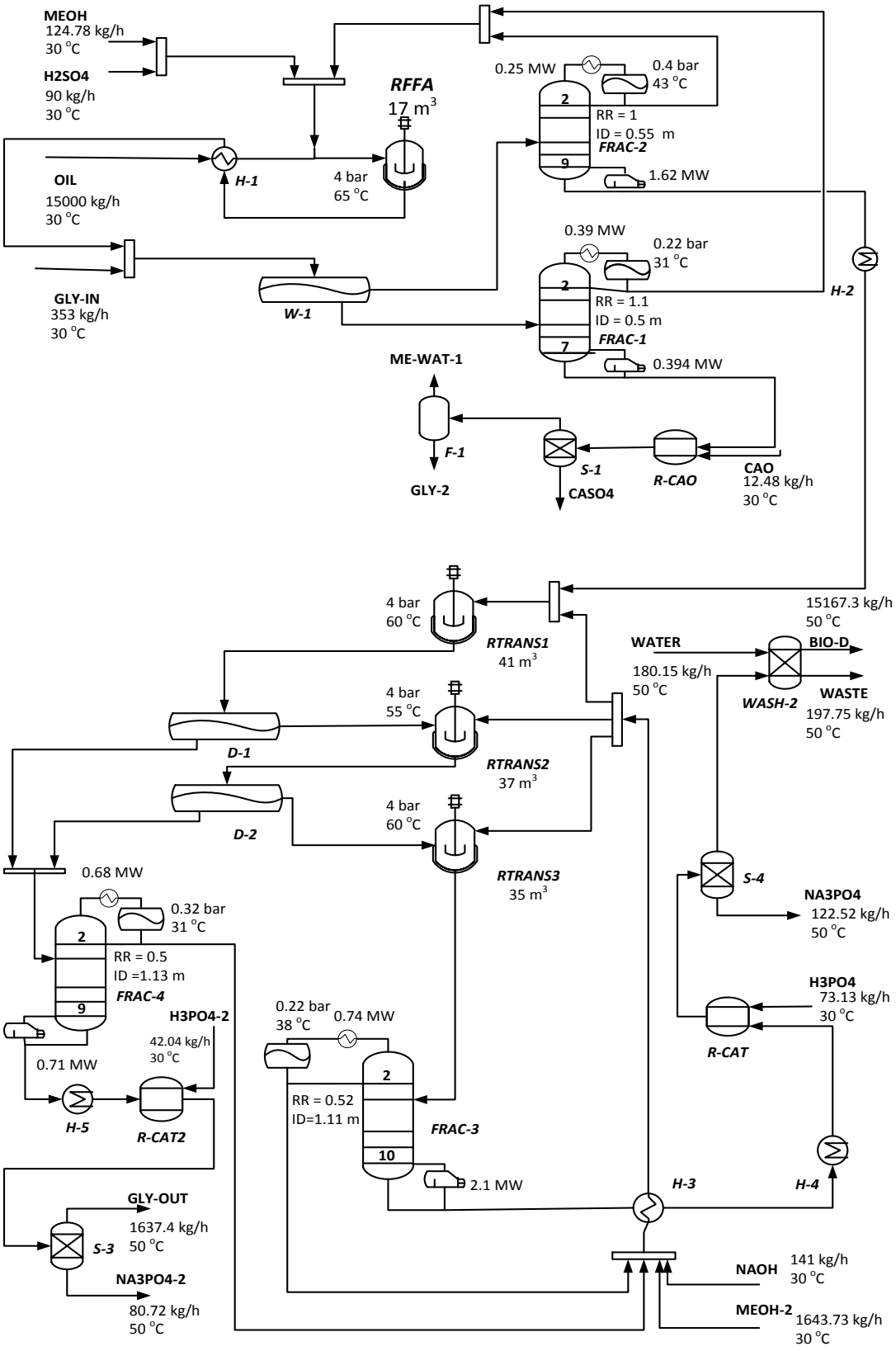

Figure 3.8 Simplified biodiesel production process from WCO (ID = internal diameter & RR = reflux ratio).

3.4.1 Level 1.1. Define PWC Objectives

In this level, PWC objectives are formulated from the operational point of view. Classically, these include production rate, product purity, process/equipment constraints, safety concerns and environmental regulations. In case of any conflict between plantwide objectives and unit-wise objective, the former should be given priority. For the biodiesel process, PWC objectives are: 1) stable production rate at normal operation with quick and smooth performance in the presence of disturbances, 2) product quality as per EN 14214 standards (biodiesel > 96.5%), 3) maintaining distillation temperatures below 250^{o}C and 150^{o}C for the columns processing biodiesel and glycerol respectively, to avoid thermal degradation, and 4) maintaining required ratio of methanol to oil (6:1 molar ratio at normal condition) and methanol split fraction to the 3 transesterification reactors (RTRANS1:RTRANS2:RTRANS3 = 0.77:0.12:0.11 at normal condition based on methanol to oil molar ratio in each CSTR) in order to obtain biodiesel quality meeting EN standards. Note that different set of objectives may result in different control systems.

3.4.2 Level 1.2. Determine Control Degree of Freedom (CDOF)

Murthy Konda et al. (2006a) proposed a method to determine CDOF based on the restraining number; it is easy to apply and effective. As deduced by Murthy Konda et al. (2006a), CDOF is found by subtracting the sum of restraining numbers and redundancies from the total number of streams. Restraining number of a unit is defined as the total number of independent and overall material balances having no

associated inventory. Redundancies in the process refer to the variables that need not to be manipulated. In the chosen biodiesel process, there are a total of 108 streams (including mass and energy streams), sum of restraining numbers is 28 and redundancies is 12. Hence, CDOF = 108–28–12 = 68.

3.4.3 Level 2.1. Identify and Analyze Plantwide Disturbances

Plantwide disturbances can pose tough challenges in the normal operation of the plant. Cognizance of possible disturbances in the process is of vital importance while developing a control scheme and controller tuning. For this, the steady state simulation model can be used to investigate the effect of possible disturbances. Table 3.3 lists the anticipated disturbances during biodiesel plant operation and their effects on important quantities. PWC papers in the literature (Shen et al., 2011; Cheng et al., 2014; Zhang et al., 2012) have used the magnitude of disturbances between ±5% and ±20% in feed flow rate.

In this work, we considered up to +20% and -30% change in WCO as the availability of WCO is uncertain and shortage of supply could likely be the situation. Also, -10% change in pre-exponential factor of transesterification reactions (this may occur due to the catalyst deactivation or may arise due to the error in the kinetics estimation), is considered.

Table 3.3 Anticipated disturbances in the biodiesel process and their effects on product flow rate, fresh methanol, recycled methanol and overall conversion.

Disturbance no. with Details	Δ(product flow rate)	Δ(fresh methanol flow rate)	Δ(recycle methanol flow rate)	Δ(Overall conversion)
D1 (+10% in WCO flow rate)	10.002 %	10.453 %	9.85%	0 %
D2 (-10% in WCO flow rate)	-10.005 %	-9.447 %	-10.22%	0 %
D3 (-10% in pre-exponential factor of transesterification reactions, due to catalyst deactivation)	0 %	0 %	0 %	~0.1 %
D4 (D1 and D3 simultaneously)	10.022 %	9.64 %	9.89%	~0.1 %
D5 (D2 and D3 simultaneously)	-10.011 %	-11.74 %	-10.34%	~0.1 %
D6 (+20% in WCO flow rate)	20.023 %	19.4 %	19.5%	0 %
D7 (-30% in WCO flow rate)	-30.013 %	-29.74 %	-30.2%	0 %

It can be seen from Table 3.3 that the change in WCO leads to a nearly proportionate variation in the recycle streams and product flow rates, and that the overall conversion of WCO is almost unaffected. Performance of the designed PWC system for the disturbances in Table 3.3 is presented and discussed in Section 4.4.

3.4.4 Level 2.2. Set Performance and Tuning Criteria

In this level, settling time is selected as the criterion for performance evaluation of the control system. As a large number of control loops are involved in this process, each controller has to be tuned once the control loops are established. Flow, level and pressure controllers are tuned based on the guidelines given in Luyben (2002). The remaining controllers are tuned using the in-built Autotuner in Aspen Plus Dynamics (APD). Controllers with time lags, such as temperature and composition control loops, are tuned using the closed-loop autotune variation method in APD (Wu and Wang, 2013). Tyreus-Luyben (TL) method (Shen et al., 2011; Luyben and Luyben, 1997) is used to determine the controller tuning parameters in such loops. Firstly, the sign of process gain using open loop test is determined and a new set-point is introduced after implement a proportional control. Then the proportional gain is increased until sustained periodic oscillations are obtained. Finally, control parameters are determined as prescribed by Tyreus-Luyben by recording ultimate gain and ultimate period. For example, temperature control loop in 'RFFA': gain = 6.56 %/% and intergral time = 13.2 min for ultimate gain of 21 %/% and ultimate period of 6 min.

The controllers without time lags are tuned using the open-loop tuning method in APD; Cohen and Coon (CC) method is used to tune these control loops. For example, +5% change is introduced in the manipulated variable. Corresponding changes in the controlled variables is plotted and the required variables (such as, time delay, gain, etc) are determined. Finally, tuning parameters (i.e. controller gain, intergral time) are determined based on the correlations given by Cohen and Coon. In

this study, 'PIDIncr' is used in place of normal 'proportional-integral-derivative' (PID). 'PIDIncr' is implemented differently than 'PID'; however, they share similar features. 'PID' uses a positional algorithm to calculate the controller output from the current error and accumulated integral error, whereas 'PIDIncr' uses an incremental algorithm which calculates the change in the output as a function of the error. The implementation of 'PIDIncr' is closer to that of real industrial controllers, and it models their detailed behavior more closely. In particular there is no bump in the output when you change the tuning parameters during a dynamic simulation, whereas PID may give a bump in the output. This make PIDIncr better for tuning controllers as a simulation runs (Aspen Technology, 2014). Table 3.4 summarizes the tuning parameters used for all control loops.

Table 3.4 Control structure with tuning parameters for the biodiesel plant.

Controllers	**Controlled variable (CV)**	**Manipulated variable (MV)**	**Reasons for selection of MV**	**Controller parameters [Kc (%/%), τ_i (min)]**
Esterification section (21 controllers)				
FC100	Biodiesel production rate	Inlet oil flow (TPM) [V-14]	Heuristics (supported by simulation)	0.5; 0.3
FC101	Glycerol flow (remote set point based on H2SO4 in stream W-1-2)	Inlet glycerol flow [V-5]	Heuristics	0.5; 0.3
RC100	Methanol/FFA ratio {remote set point based on composition of FFA in stream BIO-D}	Fresh methanol flow [V-1]	Simulation	0.5; 0.3

Table 3.4 Control structure with tuning parameters for the biodiesel plant (continued).

RC101	Sulfuric acid /FFA ratio	Inlet sulfuric acid flow [V-2]	Simulation	0.5; 0.3
PC101	Condenser pressure in FRAC-2	Condenser duty in Frac-2 [V-55]	Most direct manipulator (supported by simulation & heuristics)	2; 10
PC102	Condenser pressure in FRAC-1	Condenser duty in Frac-1 [V-56]		2; 10
PC103	Pressure in F-1	Vapor flowrate [V-12]	Most direct manipulator	2; 10
TC100	Temperature in RFFA	Utility flow	ERGA	6.56; 13.2
TC101	Bottom stage temperature in FRAC-2 {remote set point}	Reboiler duty in Frac-2	ERGA	21.71; 13.56
TC102	Bottom stage temperature in FRAC-1 {remote set point}	Reboiler duty in Frac-1	ERGA	33.3; 11.3
TC103	Temperature of heater ‘H-2’ outlet	Heat duty in ‘H-2’	Most direct manipulator	22.9; 12.6
LC100	Level in RFFA	Liquid outlet flow [V-42]	ERGA	10; 60
LC101	Light phase level in W-1	Light phase outlet flow [V-6]	Simulation	5
LC102	Heavy phase level in W-1	Heavy phase flow [V-7]	Simulation	5
LC103	Reflux drum level in FRAC-2	Distillate flow [V-4]	ERGA	2
LC104	Column base level in FRAC-2	Bottoms flow [V-8]	ERGA	2
LC105	Reflux drum level in FRAC-1	Distillate flow [V-3]	ERGA	2
LC106	Column base level in FRAC-1	Bottoms flow [V-9]	ERGA	2

Table 3.4 Control structure with tuning parameters for the biodiesel plant (continued).

LC107	Level in R-CAO	Liquid outlet flow [V-10]	Simulation	10; 60
LC108	Level in F-1	Liquid outlet flow [V-13]	Heuristics (supported by simulation)	5; 60
pH100	pH of stream R-CAO-1	Inlet calcium oxide flow [V-15]	Most direct manipulator (Steady state gain)	0.5; 0.3
Transesterification section (31 controllers)				
RC200	Methanol/(TG+DG+MG) ratio {remote set point based on composition of TG in stream BIO-D}	Fresh methanol flow [V-33]	Simulation	0.5; 0.3
RC201	Sodium hydroxide/(TG+DG+MG) ratio	Inlet sodium hydroxide acid flow [V-2]	Simulation	0.5; 0.3
PC203	Condenser pressure in FRAC-4	Condenser duty in Frac-4 [V-58]	ERGA	2; 10
PC204	Condenser pressure in FRAC-3	Condenser duty in Frac-3 [V-57]	ERGA	2; 10
TC200	Temperature in RTRANS1	Utility flow	ERGA	13.87; 19.8
TC201	Temperature in RTRANS2	Utility flow	ERGA	12.11; 13.2
TC202	Temperature in RTRANS3	Utility flow	ERGA	15.54; 26.4

Table 3.4 Control structure with tuning parameters for the biodiesel plant (continued).

TC203	Bottom stage temperature in FRAC-4 {remote set point based on composition of glycerol in stream GLYC-OUT}	Reboiler duty in Frac-4	Most direct manipulator (Largest steady state gain)	21.22; 9.62
TC204	Bottom stage temperature in FRAC-3 {remote set point}	Reboiler duty in Frac-3		23.23; 13.83
TC205	Temperature in R-CAT	Heat duty in 'H-4'	Most direct manipulator	9.63; 17.23
TC206	Temperature in R-CAT2	Heat duty in 'H-5'	Most direct manipulator	13.63; 7.92
LC200	Level in RTRANS1	Liquid outlet flow [V-16]	ERGA	10; 60
LC201	Light phase level in D-1	Light phase outlet flow [V-19]	Simulation	5; 60
LC202	Heavy phase level in D-1	Heavy phase flow [V-17]	Simulation	5; 60
LC203	Level in RTRANS2	Liquid outlet flow [V-23]	ERGA	10; 60
LC204	Light phase level in D-2	Light phase outlet flow [V-24]	Simulation	5
LC205	Heavy phase level in D-2	Heavy phase flow [V-18]	Simulation	5
LC206	Level in RTRANS3	Liquid outlet flow [V-25]	ERGA	10; 60
LC207	Reflux drum level in FRAC-4	Distillate flow [V-29]	ERGA	2
LC208	Column base level in FRAC-4	Bottoms flow [V-30]	ERGA	2

Table 3.4 Control structure with tuning parameters for the biodiesel plant (continued).

LC209	Level in R-CAT2	Liquid outlet flow [V-27]	Simulation	10; 60
LC210	Reflux drum level in FRAC-3	Distillate flow [V-31]	ERGA	2
LC211	Column base level in FRAC-3	Bottoms flow [V-32]	ERGA	2
LC212	Level in R-CAT	Liquid outlet flow [V-37]	Simulation	10; 60
LC213	Light phase level in WASH-2	Light phase outlet flow [V-39]	Simulation	5
LC214	Heavy phase level in WASH-2	Heavy phase flow [V-40]	Simulation	5
pH200	pH of stream R-CAT2-1	Inlet phosphoric acid flow [V-26]	Most direct manipulator	0.5; 0.3
pH201	pH of stream R-CAT-1	Inlet phosphoric acid flow [V-36]	Most direct manipulator	0.5; 0.3
CC200	Methanol composition in stream BIO-D (active only when exceeding the limit)	Wash water flowrate [V-38]	Most direct manipulator	0.5; 0.3
SP200	Methanol split ratio to RTRANS1	Methanol flowrate to RTRANS1 [V-20]	Most direct manipulator (Steady state gain)	0.5; 0.3
SP201	Methanol split ratio to RTRANS2	Methanol flowrate to RTRANS2 [V-21]	Most direct manipulator (Steady state gain)	0.5; 0.3

3.4.5 Level 3.1. Production Rate Manipulator Selection

Selection of a suitable TPM is critical for the process to respond to the variations quickly and smoothly. This step deals with the selection of manipulated variable for varying throughput. Internal variables, such as reactor operating parameters on this path, are preferred over external variables (i.e., fixed flow followed by on demand option). In fixed flow strategy, the feed flow rate is set and controlled at a particular value. On the contrary, in on demand strategy, the production rate is directly controlled at the desired value. The decision regarding TPM can be taken using the steady state simulator. The process variable having a larger steady state gain should be the natural choice. In the biodiesel process, the reactors have to be run at optimal conditions to maximize the product formation; these optimal conditions are fixed by optimization in this case. Therefore, these parameters will not be used as TPM, and feed (WCO) flow rate is identified as the next best choice for TPM.

3.4.6 Level 3.2. Product Quality Manipulator Selection

Selection of manipulated variable for product purity is dealt with in this level. Maintaining biodiesel purity is amongst important objectives while developing a control system as it has to meet EN/ASTM standards. Accordingly, biodiesel purity and impurity levels, such as TG, DG and MG in the final product, should be monitored and subsequently controlled. Therefore, proper reaction conditions should be maintained to convert WCO completely so that its components will not end up in the final product. The critical variables for this include methanol to oil molar ratio,

reactor temperature and catalyst. The desired ratio of methanol is maintained using ratio controllers RC100 and RC200 (in Figure 3.9) through the cascade loop to maintain FFA and TG impurity, respectively, in the final product below the permissible limit.

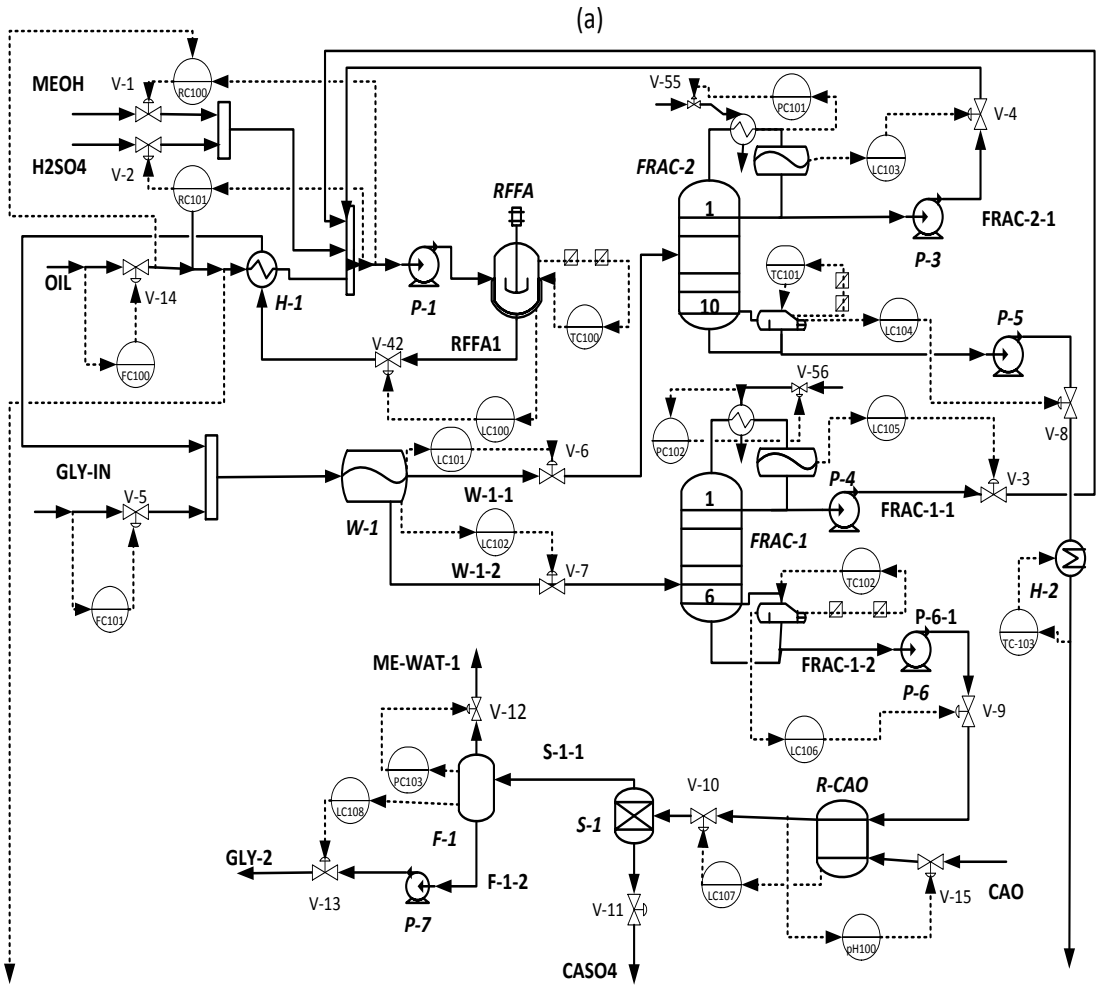

Figure 3.9(a) PWC system designed for the biodiesel production process from WCO: esterification section (note that reflux flow rates are fixed and their control is not shown).

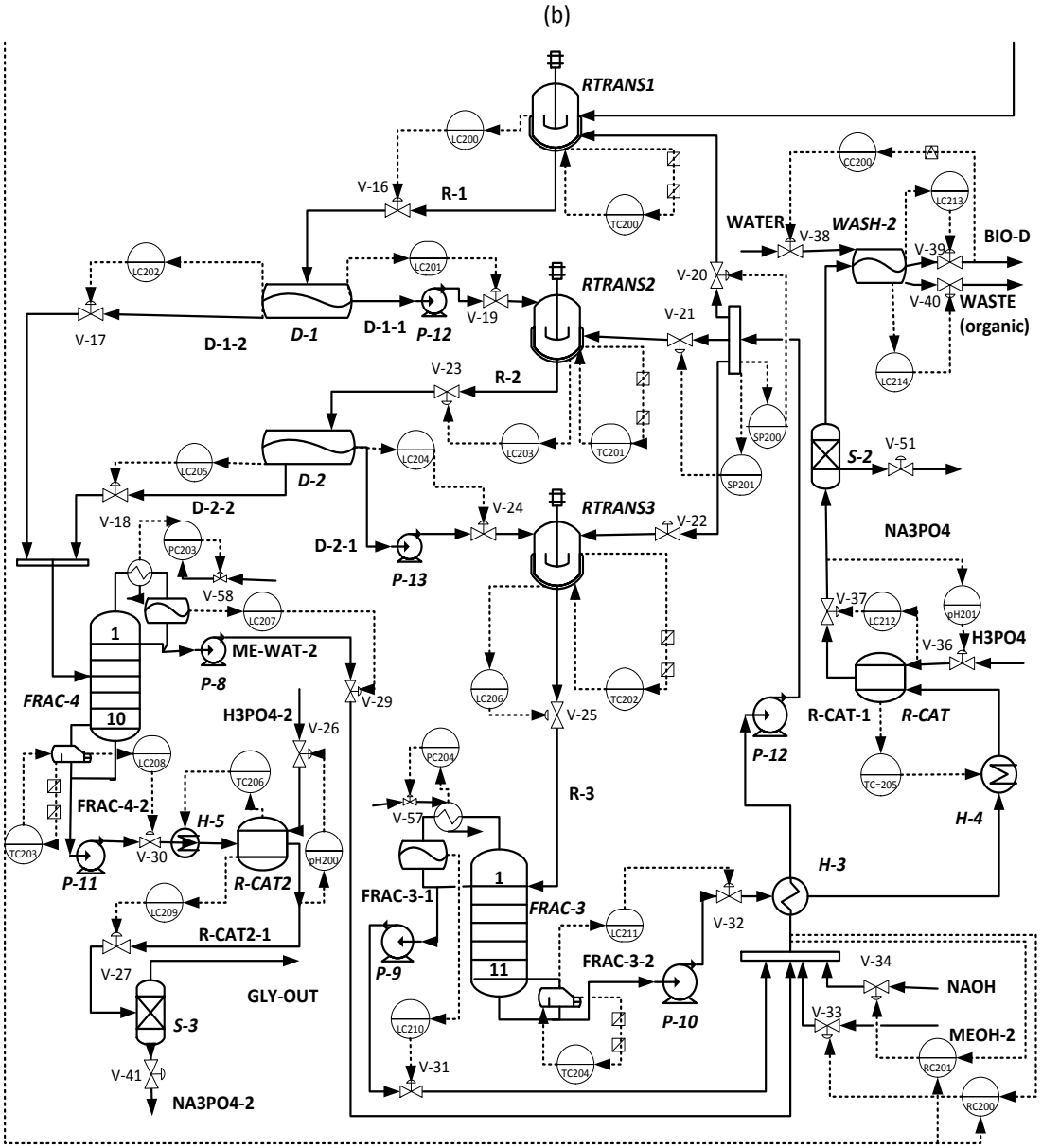

Figure 3.9(b) PWC system designed for the biodiesel production process from WCO: transesterification section (note that reflux flow rates are fixed and their control is not shown).

The three inputs to RC100 are: 1) amount of FFAs, 2) amount of methanol in the stream entering 'RFFA', and 3) amount of FFAs remained in the biodiesel. Amount of FFAs remained in the biodiesel decides the set point for 'RC100' (i.e., set

point for molar ratio of methanol to FFAs will change when the FFA content in the final product violates the permissible limit). Accordingly, fresh methanol (stream 'MEOH') to the esterification section is manipulated by the RC100 controller. Similarly, the three inputs to RC200 are: 1) amount of TG, 2) amount of methanol in the stream entering the splitter, and 3) amount of TG remained in the biodiesel. Amount of TG remained in the biodiesel decides the set point for 'RC200' (i.e., set point for 'RC200' will change when the TG in the final product violates the permissible limit). Accordingly, fresh methanol (stream 'MEOH-2') is manipulated by the RC200 controller. Methanol impurity in the biodiesel product is controlled by manipulating the wash water flow rate (controller 'CC200' in Figure 3.9).

Also, as glycerol is a valuable byproduct from transesterification section in biodiesel production, its purity should be maintained at the desired value. A cascade loop is implemented to manipulate the reboiler duty of FRAC-4 to maintain glycerol purity. Additionally, the control system is designed in such a way that the maximum temperature in FRAC-4 will not go beyond 150^{o}C to avoid glycerol decomposition. In the esterification section, glycrol (stream 'GLY-IN') is fed in small quantity to achieve the separation of unreacted sulfuric acid in the heavy phase from the phase separator 'W-1'. Later, the glycerol is recovered through 'FRAC-1', 'R-CAO', 'S-1', and 'F-1', and it can be either recycled or mixed with byproduct glycerol stream 'GLY-OUT'. In this study, the recovered glycerol is not recycled due to its small quantity. Set point of the controller 'FC101' (for glycerol flow rate) is decided based on the amount to sulfuric acid in the lighter phase.

3.4.7 Level 4.1. Selection of Manipuled Variables for More Severe Controlled Variables

In this level, process constraints related to process stability, equipments, operation, safety and the environment are dealt with. These are crucial to control as these may lead to severe operational ramifications. The important constraints in this process are:

i. Column temperatures, T_{FRAC-1} and $T_{FRAC-4} \leq 150^oC$, and T_{FRAC-2} and $T_{FRAC-3} \leq 250^oC$

These temperatures are allowed to vary within acceptable limits. The controller becomes active as and when the controlled variable (i.e., temperature) violates the limit, which is given as the remote set point for the respective controller.

ii. Respective ratios of feeds

Fresh methanol is manipulated to maintain the desired ratio of methanol using controllers RC100 and RC200. Molar ratio of methanol to FFA is 10:1 in 'RFFA', and methanol to TG, DG and MG ratio is 6:1 in 'RTRANS1', 'RTRANS2' and 'RTRANS3', at normal operation. Similarly, ratio controllers, RC101 and RC201 are also implemented to maintain the ratio of sodium hydroxide (1 wt%) and sulfuric acid (10 wt%).

iii. Methanol split ratios for the CSTRs

Controllers SP200 and SP201 are employed to maintain the split fractions (RTRANS1: RTRANS2: RTRANS3 = 0.77:0.12:0.11, at normal condition).

iv. CSTR temperatures

Reactor temperatures have to be maintained at their desired values in order to maintain WCO conversion. Aspen Plus Dynamics (V8) provides different options for reactor temperature control such as constant duty, constant temperature, condensing, evaporating, dynamics and LMTD. One of these options can be chosen depending on the application and the extent of realistic results sought from simulations. For example, the constant duty model is the most idealistic that does not reflect the consideration of heat transfer area or temperature differential. In this study, the LMTD option is used to yield more realistic results that uses a log-mean temperature difference. The assumed overall heat transfer coefficient (U) is 0.4 kW/m^2-K for both cooling water (at 30^{o}C for heat removal) and hot water (at 80^{o}C for heat addition). The heat capacity is taken to be 4.2 kJ/kg-K for both cooling water and hot water. The area (A) for heat transfer, based on half of the lateral surface area of the cylindrical reactor, is 24.07 m^2, 43.9 m^2, 40.98 m^2 and 40.8 m^2 for RFFA, RTRANS1, RTRANS2 and RTRANS3, respectively. Therefore, their UA is 9.63 kW/K, 17.56 kW/K, 16.39 kW/K and 16.31 kW/K, respectively. For the initial steady state, the heat duty found from APD simulation is 0.32 GJ/h, 0.68 GJ/h, -0.97 GJ/h and 0.64 GJ/h for RFFA, RTRANS1, RTRANS2 and RTRANS3, respectively. The utility outlet temperature is 70^{o}C, 65^{o}C, 45^{o}C and

65^{o}C for these reactors, respectively. Accordingly, the required utility flow rate is 7619 kg/h, 10794 kg/h, 15397 kg/h and 10159 kg/h for RFFA, RTRANS1, RTRANS2 and RTRANS3, respectively. Effective relative gain array (ERGA) (Xiong et al., 2005), described below, is employed to determine the suitable CV-MV pairings for the reactors and distillation columns.

Xiong et al. (2005) presented a dynamic loop pairing criterion for decentralized control of multivariable processes, where the control loop pairing procedures of the relative gain array (RGA) are extended to develop the new method 'ERGA' which reflects dynamic loop interactions under finite bandwidth control. Other recent method for such pairing are 'Dynamic input-output pairing matrix' by Moaveni and Khakisedigh (2008) and a method based on the fuzzy analysis of a linear cross-correlation between the output and the inputs by Potts et al (2015). In addition to steady state gain, ERGA also utilizes the bandwidth (i.e. the range of frequencies within a given band) information of the process open loop transfer function. Also, this method is simple and easy to implement. ERGA method is summarized as follows; refer to Xiong et al. (2005) for further details.

1) Obtain open loop transfer functions (TF), say, FOPTD model: $G(s) = \frac{Ke^{-\theta s}}{\tau s+1}$

2) Determine bandwidth from TF.

3) Find effective gain matrix E = G(0)×Ω where

$$E = \begin{bmatrix} e_{11} & e_{12} & \cdot\cdot & e_{1n} \\ e_{21} & e_{22} & \cdot\cdot & e_{2n} \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ e_{n1} & e_{n2} & \cdot\cdot & e_{nn} \end{bmatrix},$$

$$G(0) = \begin{bmatrix} g_{11}(0) & g_{12}(0) & \cdot\cdot & g_{1n}(0) \\ g_{21}(0) & g_{22}(0) & \cdot\cdot & g_{2n}(0) \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ g_{n1}(0) & g_{n2}(0) & \cdot\cdot & g_{nn}(0) \end{bmatrix} \text{ and}$$

$\Omega = \begin{bmatrix} \omega_{B,11} & \omega_{B,12} & \cdot\cdot & \omega_{B,1n} \\ \omega_{B,21} & \omega_{B,21} & \cdot\cdot & \omega_{B,21} \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \omega_{B,n1} & \omega_{B,n1} & \cdot\cdot & \omega_{B,nn} \end{bmatrix}$, which denotes the bandwidth matrix (i.e. matrix having bandwidth value for the particular input-output pairing) calculated based on the individual elements of G(s).

4) Find ERGA, $\phi = E \times E^{-T}$,

where $\phi = \begin{bmatrix} \phi_{11} & \phi_{12} & \cdot\cdot & \phi_{1n} \\ \phi_{21} & \phi_{22} & \cdot\cdot & \phi_{2n} \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \phi_{n1} & \phi_{n2} & \cdot\cdot & \phi_{nn} \end{bmatrix}$

Finally, the pairing is selected according to the following rules; (i) corresponding ERGA elements closest to 1 should be preferred, (ii) the positive Niederlinski index (NI) $\left(= \frac{det(G(0))}{\prod_{i=1}^{m} g_{ii}(0)}\right)$ is required, (iii) selected pair (i.e., corresponding ERGA element) should be positive, and (iv) the input-output pair having a large ERGA element should be avoided.

3.4.8 Level 4.2. Selection of Manipuled Variables for less Severe Controlled Variables

Primarily, this step decides the level and pressure control loops. Levels along the primary process path should be stable and properly controlled as they are often integrating. To achieve a self-consistent level control, the control of levels before TPM should be in the direction opposite to flow, whereas the level controls after the TPM should be in the direction of flow. Therefore, in this study, the levels in the primary process path should be controlled in the direction of flow to obtain a self-

consistent control structure for the selected TPM fixed (feed) flow. Although the P-only controller may suffice to obtain a satisfactory performance, PI controller is implemented in some level control loops in reactors to attain the tight control. A tight level control in reactors is important as it can affect reaction rates (Luyben, 2002). Also, a proper level control in phase separators and in columns is necessary. In all distillation columns, the level in the reflux drum and column base is controlled using distillate flow and bottoms flow respectively. This is in accordance with heuristics that the level should be controlled so that the disturbances are directed away from the primary process path. Also, based on heuristics, the control of level in the reflux drum using the reflux flow rate is not appropriate as the columns in the biodiesel process are operating at smaller reflux ratios. Additionally, this is also in agreement with the Richardson's rule, which states that an inventory variable should be controlled with the manipulated variable that exerts the largest effect on it within that unit.

The liquid level in the respective reflux drums is controlled using distillate flow rates (valves V-3, V-4, V-29 and V-31 in Figure 3.9). In Aspen Plus Dynamics, reflux flow rate is kept constant by default. There is no strict need to install the reflux pump, valve and flow controller for simulation purpose. In the real physical system, these would have to be installed. The reflux flow can be manipulated as per the requirement (e.g., composition control by manipulating reflux ratio or fixing feed to reflux etc). Also, we did not encounter any difficulty in the disturbance rejections with keeping the reflux flow rate constant. Therefore, other options such as controlling reflux ratio or reflux to feed ratio, have not been explored. Also, top stream from all distillation columns is almost pure methanol, whose separation is easy due to the significantly larger difference in relative volatility. The liquid levels

in reactors and phase separators are controlled using liquid outlets, as shown in Figure 3.9. The pressure in all distillation columns is controlled using respective condenser duty; these are verified using dynamic simulations. These pairings are also in agreement with the pairings resulted from ERGA analysis, described in the previous section. The pressure in flash evaporator is controlled by manipulating the overhead vapor flow and the level is controlled using bottom liquid flow rate.

3.4.9 Level 5.0. Control of Unit Operations

This step, in particular, deals with the control of individual unit operations. It is done before testing component material balances as some component inventory loops can be implicitly satisfied in this level. Basic control of the most common processes is well established as given in Luyben (2002). In the previous section, all level and pressure control loops are already decided. Temperature control loops in CSTRs and distillation columns are also decided in level 4.2. In the biodiesel process, dual composition controls are not required in any column as the top product is methanol, which is reused in the process. Simulation results indicate that the unit operations are well regulated. The pH of the outlet stream of the neutralization reactor is controlled using inlet calcium oxide in R-CAO and using inlet phosphoric acid in both R-CAT and R-CAT2.

3.4.10 Level 6.0. Check Component Material Balances

It is necessary to ensure that the component inventory is well regulated. This means that the accumulation of the components in the entire plant with the control

structure developed so far is zero or negligible. An overall accumulation of all components in the plant should be calculated and observed. If required, unit-wise accumulation can be determined. This can be analyzed preparing a 'Downs Drill' table (see Table B.1 in the Appendix B). Negligible accumulation suggests that the inventory is well regulated.

3.4.11 Level 7.0. Effects of Integration

The dynamics of the process should be studied for the anticipated disturbances, both with and without recycles closed; see Murthy Konda et al. (2005) for more details on this. It is done by observing the overall accumulation profile of WCO in the complete plant and the effect on important parameters such as conversion and production rate. Figure 3.10 shows that the accumulation profiles of WCO with and without recycle closed do not deviate too much. From the dynamic simulations, no significant change is noticed in terms of settling time of biodiesel flow rate when recycles are closed. This suggests that plant dynamics are not significantly affected when recycles are closed or opened. Conversion and product flow rate are found to be unaffected after closing the recycles. This is mainly due to the parameters affecting these, such as temperature and methanol to oil ratio in CSTRs are already set for control in the previous steps. Also, as found in level 2.1, the change in WCO leads to proportionate variation in the recycle streams. Therefore, it can be safely assumed that the effects of integration are not severe, and hence further modification is not necessary in the developed control system.

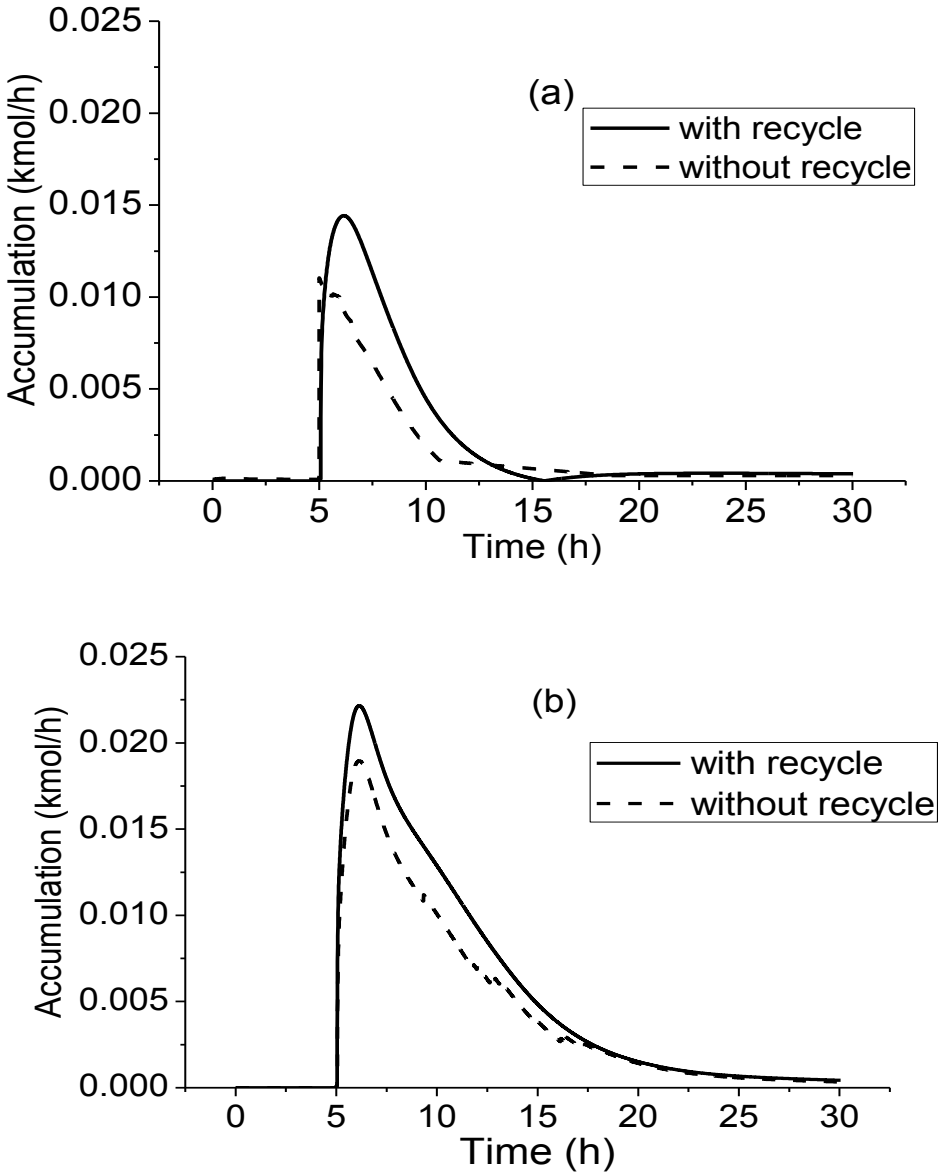

Figure 3.10 WCO accumulation with and without recycle (a) due to disturbance D6 and (b) due to disturbance D7.

3.4.12 Level 8.0. Enhance Control System Performance with Remaining CDOF

If required, remaining CDOFs can further be utilized to improve the performance of developed control structure. For the complete biodiesel plant, the developed control system appears to be satisfactory and so no modifications are

warranted. The resulted control structure from the eight-level IFSH methodology uses 52 out of the available 68 CDOF, and it is shown in two plots for clarity; Figures 3.9(a) and 3.9(b) present the control structure for esterification section and transesterification section, respectively. The percentage opening of control valves is set to be about 50% at nominal operation. However, valve openings may marginally deviate from this as was found in Zhang et al (2012). In this process, the valve openings deviated between 49-51%. This is due to a pressure driven simulation (i.e. the simulation model based on pressure-flow solver, where pressure depends on upstream conditions) used in this study.

With the application of methodical PWC methodology i.e. IFSH, location of TPM, presence of snowball effect, accumulation profile, recycle dynamics and quality controllers are meticulously identified which may not have been identified with normal base layer simple control methods. Due to the large number of control loops present in this PWC scheme, individual control loops are not assessed in terms of conventional time domain performance specification such as overshoot, rise time and integral error indices. Besides, the PWC system performance should be analyzed from a plantwide perspective. The criteria for the quantification of control system's performance should be reliable and easy, and essentially they should describe several factors such as an economic index, smoothness and stability. Vasudevan and Rangaiah (2010) proposed several criteria for the performance assessment of PWC systems. This work uses some of these, viz settling time (indicative of smooth and safe operation of the plant), DPT (denotes an indirect economic index) and overall TV (indicator of the control efforts required for PWC structure to attain stable operation) for the performance evaluation, as discussed in Section 4.4. These are explained in brief as follows;

i. **Process settling time based on plant production rate.** Settling time based on plant production rate is a measure of time taken by PWC system to reach the production of the main product to the steady state, after the disturbance(s) is introduced. It is one of the most important factors for the smooth and safe operation of the plant. Smaller settling time is desired for an effective PWC system.

ii. **Deviation from production target (DPT).** DPT is an indirect economic indication in terms of production rate. Additionally, it shares the advantages of dynamic disturbance sensitivity and also indicates the plant economics, which makes it an attractive and a more complete performance indicator. Smaller DPT means that the PWC system is better and effective. Vasudevan and Rangaiah (2010) defined DPT as:

$$DPT = \int_0^{t_s} (P_A - P_T) dt \tag{3.12}$$

where P_A is actual production rate, P_T is production target and t_s is settling time.

iii. **Total variation (TV) in manipulated variables.** TV is an indicator of the control effort required for PWC system to attain the steady state after a disturbance. Smaller TV indicates the smoothness of the manipulated input signal, and minimal control effort required to attenuate the effects of any disturbance(s). The advanced features of rigorous process simulators make it convenient to save the required data, including manipulated variable data in percentages at regular intervals, from which TV can be easily computed to

assess the performance of PWC system. Overall TV in manipulated variables is calculated by summing TVs of all 52 individual controllers; it gives TV from the plantwide perspective. All the manipulated variables are expressed in percentages, for example, the change in reboiler duty is taken as % change in reboiler duty (and not in GJ/h). This is essential since computing overall TV would be inconsistent if the manipulated inputs are expressed in their actual units, for example, flow rate (kg/h) and duty (GJ/h). Vasudevan and Rangaiah (2010) defined TV as:

$$TV = \int_0^{t_s} \left|\frac{du}{dt}\right| dt \tag{3.13}$$

which can be approximated for discrete values of manipulated variable, u(t) as;

$$TV = \sum_0^{\infty} |u(t+1) - u(t)| \tag{3.14}$$

3.5 Development of Operator Training Simulator (OTS) for Biodiesel Process 1

Figure 3.11 shows the methodology followed in the OTS development. OTS uses the optimal parameters and the PWC structure found the earlier sections. In principle, the OTS consists of a computer system which includes one or more trainee station(s), one field operator station, and one instructor station, as described in Section 1. The centre of the OTS workstation will be the instructor station that functions as simulator engine, and instructor tools that interconnects with other work stations namely operator station and field operator station.

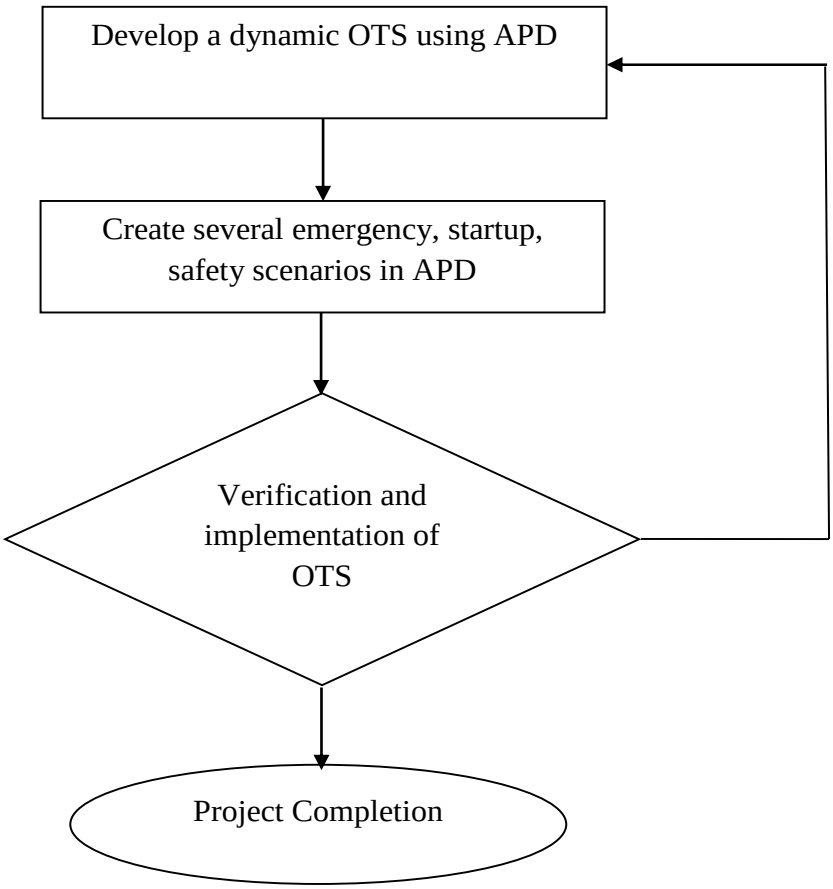

Figure 3.11 Flowchart on the general framework of the OTS.

Simulator model will be loaded from the instructor station and transmitted to both operator and field operator stations. DCS can be emulated, stimulated or partially stimulated that acts as a human machine interface (HMI) and is made available on the operator station with the mentioned simulator model to convey similar information, features, and functionalities as of the actual DCS system. Graphical representations of the field operated device such as block valve, local panel, etc is located on the filed operator station to provide the interface in operating the said devices which commonly cannot be operated from control room or DCS. However, in the absence of actual/emulated/stimulated/partially stimulated DCS, a standalone OTS is investigated in this study, where instructor station and operator station is the same. This is the simplest and cheapest mode of OTS; however, it is

probably the least effective among all other modes. The scope of this study is to show applicability of APD in OTS development for the complex biodiesel process for varieties of scenarios, which is the core of OTS. Therefore, HMI development for instructor or operator is not focused on in this study.

There are 3 main steps before using Aspen OTS Framework. Firstly, the process is simulated in Aspen Plus. Secondly, suitable control strategy is employed in APD. Thirdly, each training scenario is created in APD by writing the tasks. It is then accessed through Aspen OTS framework, which enables a large dynamic simulation to run in real time using parallel processing and also enables the various components of OTS to link to the simulation via OPC. It is possible to split the simulation into smaller partitions, each with its own integration step size and running in parallel on a different CPU/core, which helps simulation to run in real time as well as at increased speed. Aspen OTS framework can be used to identify the name and location of the partitions, make stream and control signal connections, publish tags, launch simulation cases, run and synchronize the partitions, exchange stream data between them, and display simulation variables and commands via OPC (Aspen OTS Framework: Help: Aspen Technology: Cambridge, MA).

Figure 3.12 shows the snapshot of the developed OTS. Controller faceplates are arranged so that all individual controllers can be monitored simultaneously. Controller modes, transient profiles (i.e. historian), controller tuning, CV-MV limits can be accessed through the respective faceplate. Other variables can be seen from ‘Process Flowsheet Window’ (Figure 3.12). Training scenarios can be (de)activated

through ‘Contents of Flowsheet’ window in Figure 3.12; ‘Simulation Messages’ window shows simulation status.

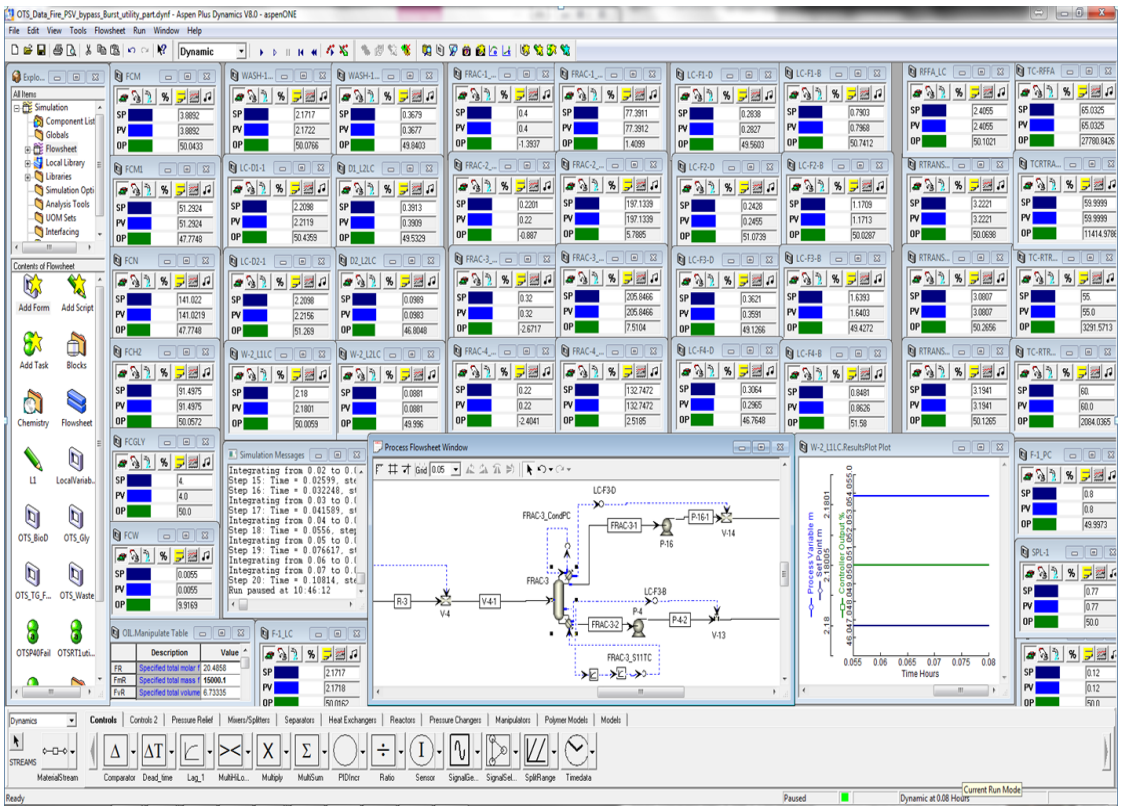

Figure 3.12 Snapshot of the developed OTS.

In OTS, a dynamic simulation is typically synchronized to run in real time. The simulation is a replica of a plant continuously generating time series data, responding to operator actions, instructor initiated upsets and DCS actions (if external controls are being used). The simulations for operator training are mostly very detailed containing all equipment items in the plant including items not normally included in an engineering study model (such as instruments and spare pumps). Consequently, these simulations are very large and include operations having fast dynamics and slow dynamics as well, e.g. compressors (fast dynamics) and distillation columns (slow dynamics). The integration size must be small catering

to the fast dynamics for accuracy. Running such a simulation on a single processor can lead to mismatch between simulation time and real time due to the limited capability of a single processor. A suitable OTS framework must be able to cope with this by some means. Using Aspen OTS Framework, it is possible to split the simulation into smaller partitions, each with its own integration step size, and each running in parallel on a different CPU/core.

The Aspen OTS Framework enables users to configure the partitions, and it manages the synchronization and data exchange among the partitions during runtime. However, it is essential to tear the streams downstream of a valve. The torn stream results in a product stream with a fixed boundary pressure in the source partition and a feed stream with a fixed flow, temperature and composition in the destination partition. The method of partitioning is illustrated in the following example (Figure 3.13), taken from Aspen OTS Framework's help (Aspen Technology, 2013). In Figure 3.13, stream 2 is cut resulting in two partitions of roughly the same size. The resulting flow sheet on the left hand side will have a product stream 2 with pressure specified. On the right hand side of the flow sheet, feed stream 2 will have flow rate, temperature and composition (and not pressure) specified. Because of the pressure/flow network, it is necessary to ensure that both the partitioned simulations are synchronized in time, with connecting stream variables updated as frequently as possible, e.g. every integration step.

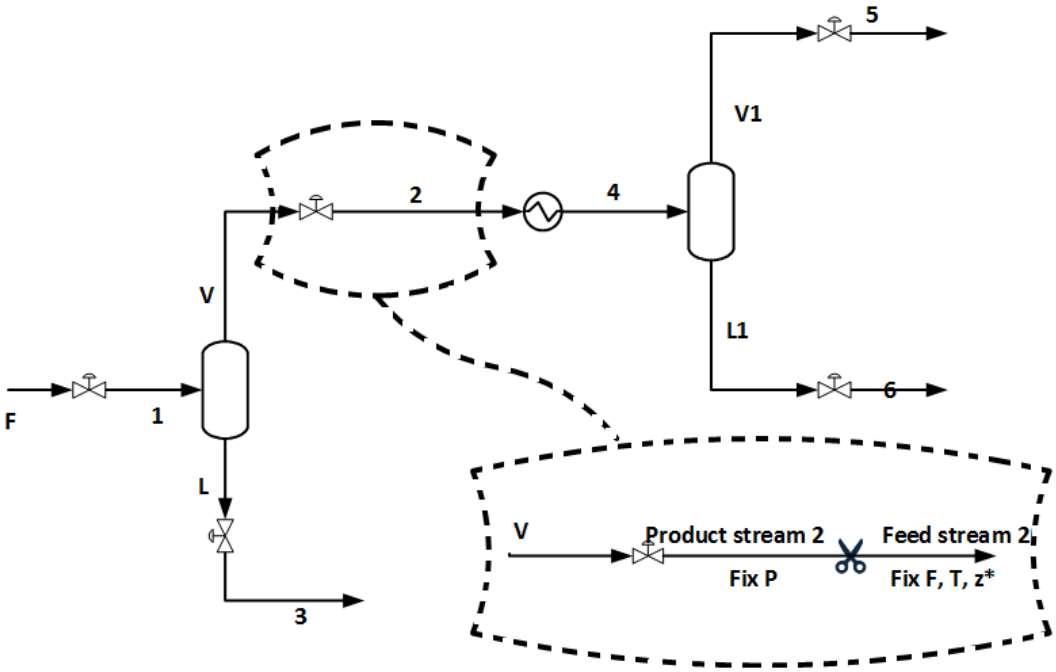

Figure 3.13 Partitioning of the process flow sheet.

The breaking of a stream (e.g. '2' in the above example into product stream 2 and feed stream 2) will result in the downstream variables: flow *(F)*, temperature *(T)* and composition (z^*) lagging behind the corresponding upstream values by one integration time step, and the upstream pressure lagging behind the downstream pressure *(P)*. Even this small lag may result in unstable oscillations. These oscillations can be eliminated if the flow copied to the downstream partition is updated using the flow/pressure derivative as;

$$F_{down} = F_{up} + \frac{\partial f}{\partial P}\left(P_{up} - P_{down}\right) \tag{3.15}$$

$\frac{\partial f}{\partial t}$ is calculated by the upstream valve using differential pressure flow equation:

$$f = Cv\sqrt{\Delta P} \tag{3.16}$$

$$\frac{\partial f}{\partial t} = \frac{1}{2}\frac{Cv}{\sqrt{\Delta P}}$$

(3.17)

Substituting Cv in Eq. (3.17):

$$\frac{\partial f}{\partial t} = \frac{1}{2}\frac{F}{\Delta P}$$

(3.18)

$\frac{\partial f}{\partial t}$ is calculated from the upstream valve using Eq. 3.18. The pressure drop of the source partition's upstream valve is used to calculate the flow/pressure derivative for each connecting stream ensuring the stability of the pressure/flow network. The partition must be done immediately downstream of a valve as the Aspen OTS Framework uses the valve in the source partition to calculate the stream's pressure-flow derivative.

Setting simulation speed, pause, resume etc can be done using Aspen OTS Framework. Figures 3.14, 3.15, 3.16 show the snapshots of OTS with flowsheet partitioned. Right bottom section, left section and right top section show esterification section, transesterification section and OTS Framework, respectively. In Figure 3.14, two partitions, namely 'OTS_Data_Fire_PSV_bypass_Burst _Utility_part_1' (i.e. esterification section) and 'OTS_Data_Fire_PSV_bypass_Burst _Utility_part_2' (i.e. transesterification section) are synchronized using Aspen OTS Framework (see highlighted part in Figure 3.14). In Figure 3.15, output of first partition (i.e. esterification section) 'str1' is connected with second partition (i.e. transesterification section) 'str2' (see highlighted part in Figure 3.15) to be synchronized. All required variables can be tagged to be able to monitor them and publish them (for example, see highlighted part in Figure 3.16). Step size for either/both partition(s) can also be changed according to the fast or slow dynamics.

As shown in these Figures, OTS speed can be enhanced or reduced by changing ‘Real time factor’. Also, data transfer rate can be increased or decreased by changing ‘Data transfer interval’ (see highlighted part in Figure 3.14). Figure 3.17 shows interface for a complete process in APD.

The scenarios for which OTS training is to be carried out should created in APD by writing the ‘Task’. An example of task writing is depicted for startup of FRAC-3, in the Appendix C. The results are discussed in Section 4.5. The scenario, written as a ‘Task’, has to be first compiled and then activated. When OTS is run, the scenario plays out at the time specified while creating the scenario in the ‘Task’. Alternatively, direct change can be made into the simulation to impart some faults. Several scenarios, such as equipment malfunctions, fire, pressure safety valves, bursting disks, interlocks and startup-shutdowns etc, can be created and tested using this OTS. These are described in section 4.4.

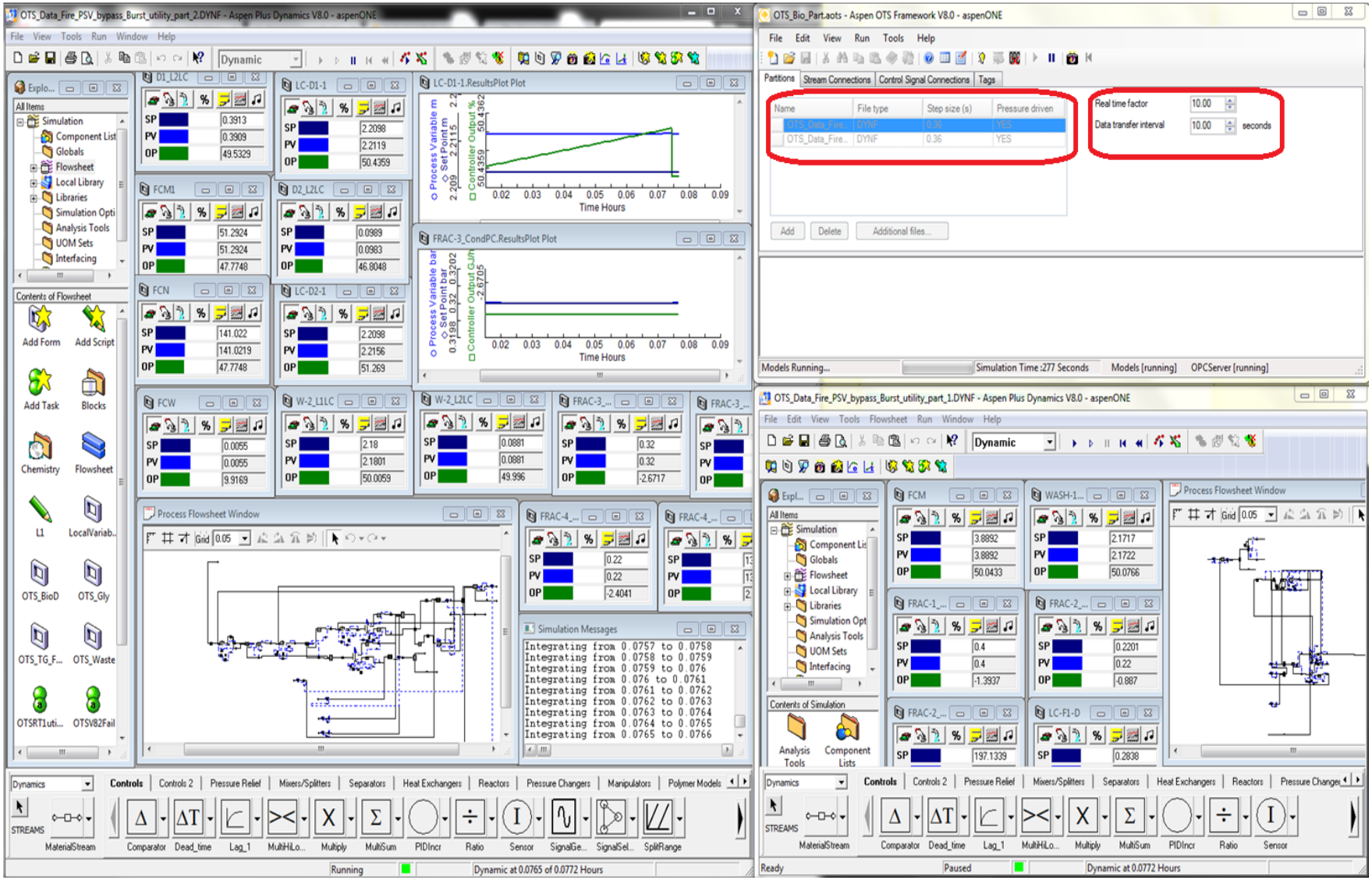

Figure 3.14 Snapshot of the developed OTS with flowsheet partitioned (Two partitions are synchronized).

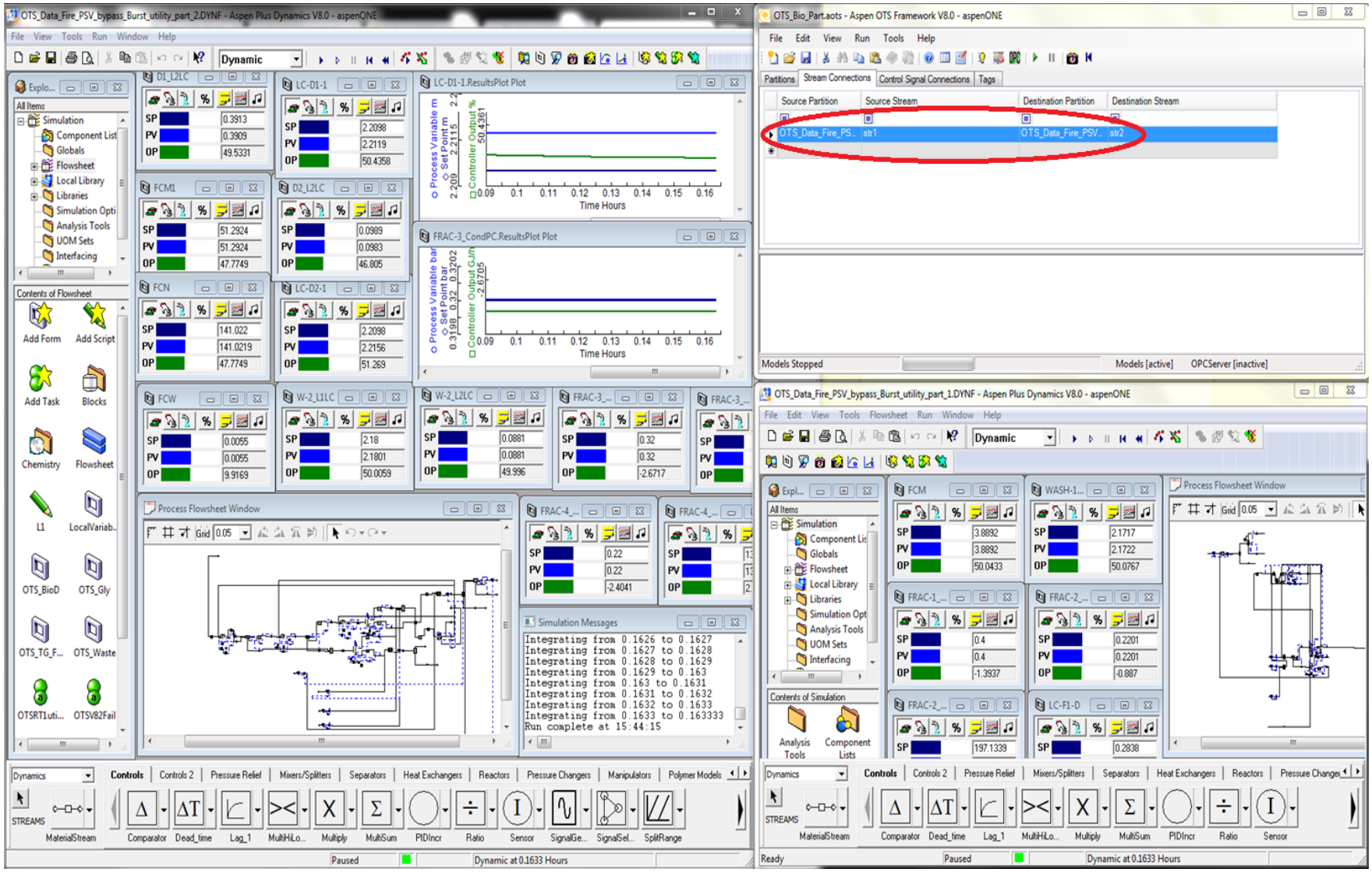

Figure 3.15 Snapshot of the developed OTS with flowsheet partitioned (Streams of two partitions are connected).

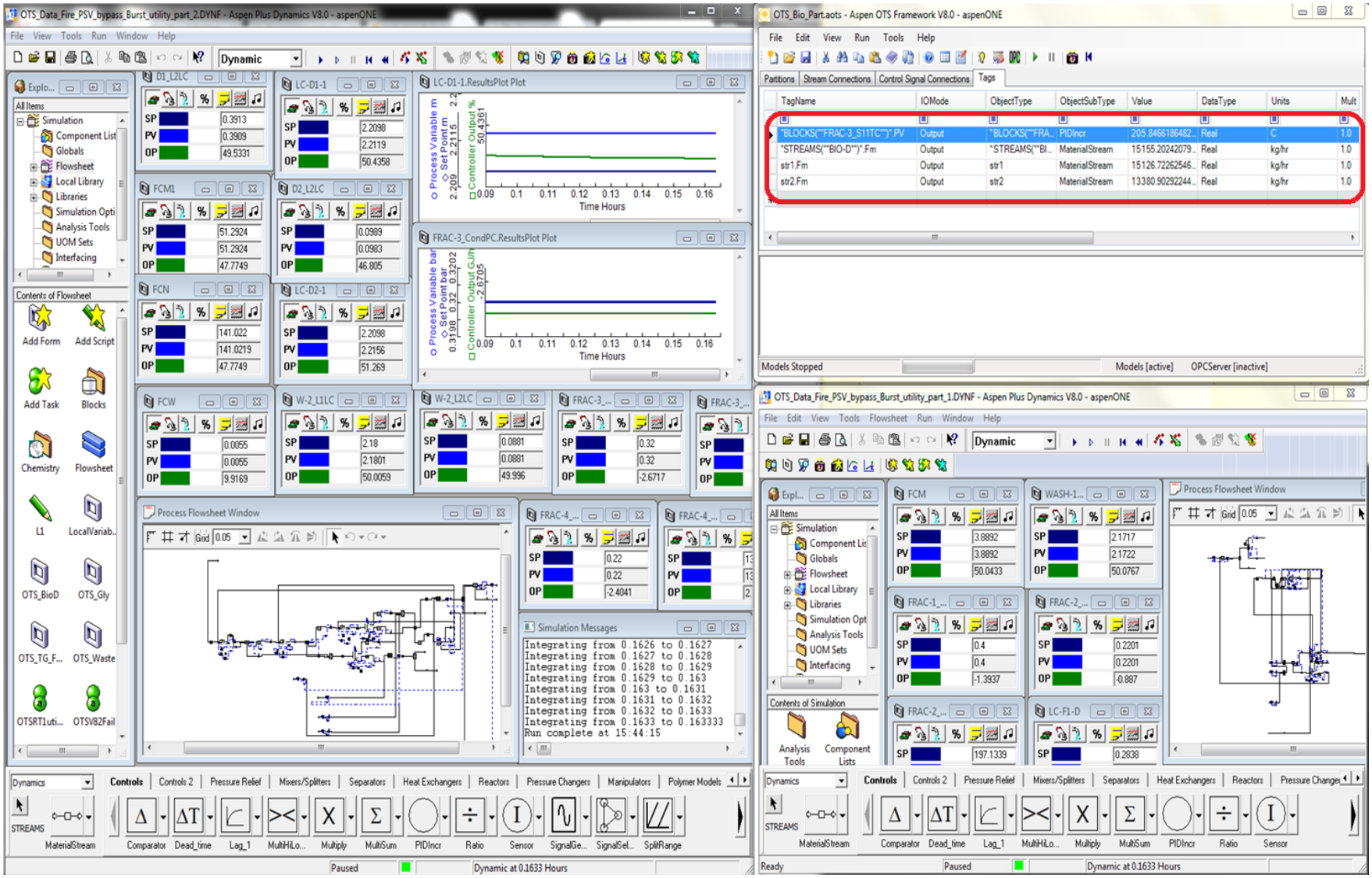

Figure 3.16 Snapshot of the developed OTS with flowsheet partitioned (Few tags are published).

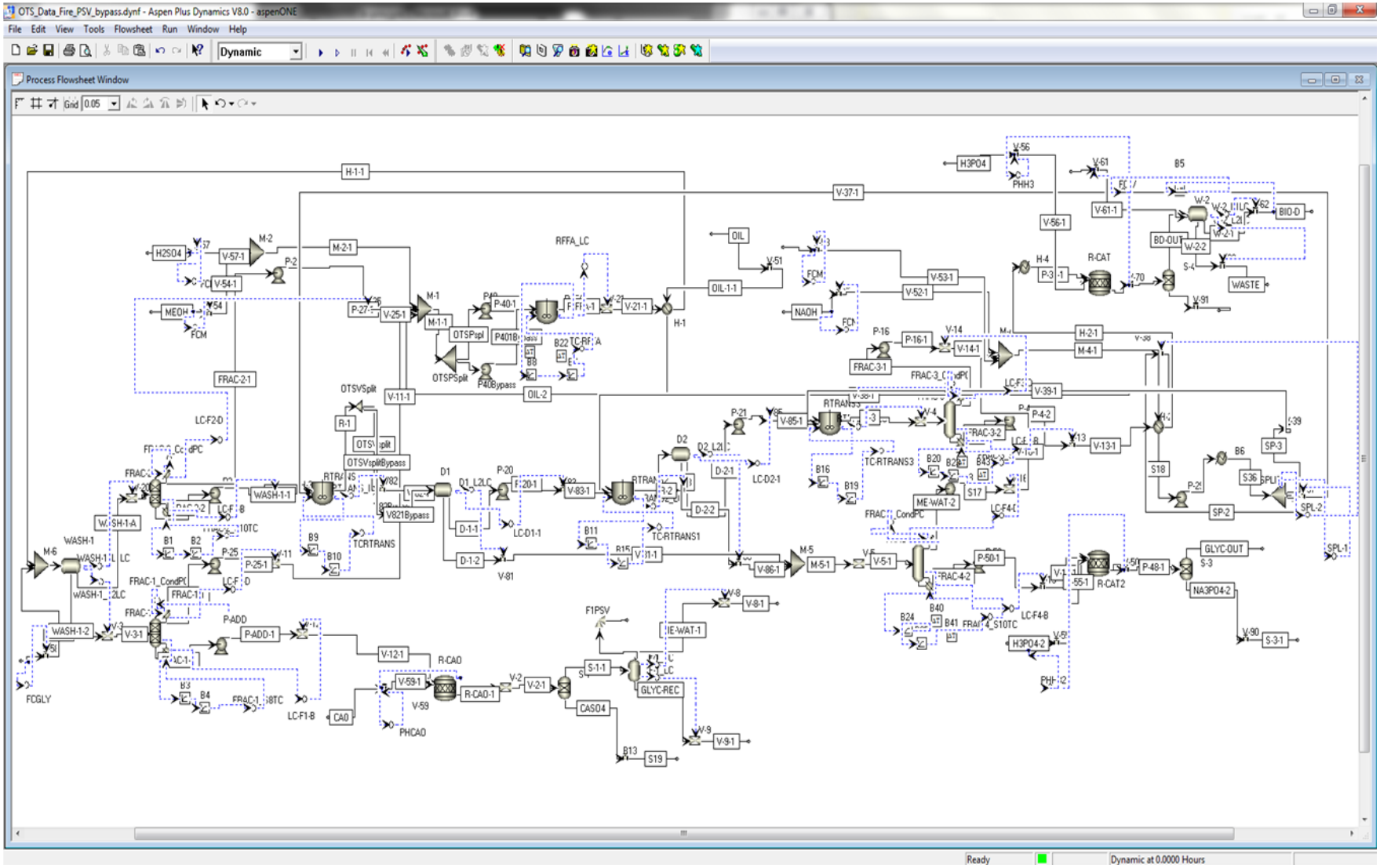

Figure 3.17 Complete process interface in APD.

3.6 A Hazard and Operability Study of Biodiesel Process 1

A hazard and operability study (HAZOP) is a structured and methodical examination of a non-existing or existing process in order to identify and evaluate problems that may indicate risks to plant-personnel or -equipment, or prevent efficient process operation. Typically, it is carried out by a suitably experienced multi-disciplinary team. The HAZOP technique aims to stimulate the imagination of HAZOP team members to identify possible hazards and operability issues.

As per our resources, a preliminary HAZOP analysis for biodiesel production from WCO (Figure 3.9) is carried out based on HAZOP Guidelines (2008), to understand the risks associated with the process. HAZOP analysis is one of the important analyses, viz. construction safety, fire safety, Functional Hazard Analysis (FHA), transport, emergency plan, and safety management system. The objective of this analysis is to systematically examine the proposed design, which should be done before the physical construction. Possible hazards and operational problems can be prevented or reduced by redesign of suitable operating procedures. Plant items in the process flowsheet are evaluated by applying appropriate guide words. Potentially hazardous situations and their ramifications are then estimated. Preventing measures to avoid or reduce the undesirable situations are also recommended. The findings of the step by step procedure and the recommendations are organized in the HAZOP minute sheet (see Appendix D). Figure 3.18 presents HAZOPed process diagram for biodiesel production from WCO. The important recommendations from this analysis are:

Rec #1

Install high flow alarm on feed line.

Rec #10, #24, #52 & #60

Install high level alarms on the column to ensure that the operating efficiency is maintained by avoiding the flooding of reboiler outlet.

Rec #8, #16, #22, #30, #34, #42, #50, #56, #58, #64, #66

Install high pressure and high temperature alarms on columns and reactors to prevent overheating.

Rec #15, #29, #57 & #65

Investigate the need for protection against air suck back into the column on cooling.

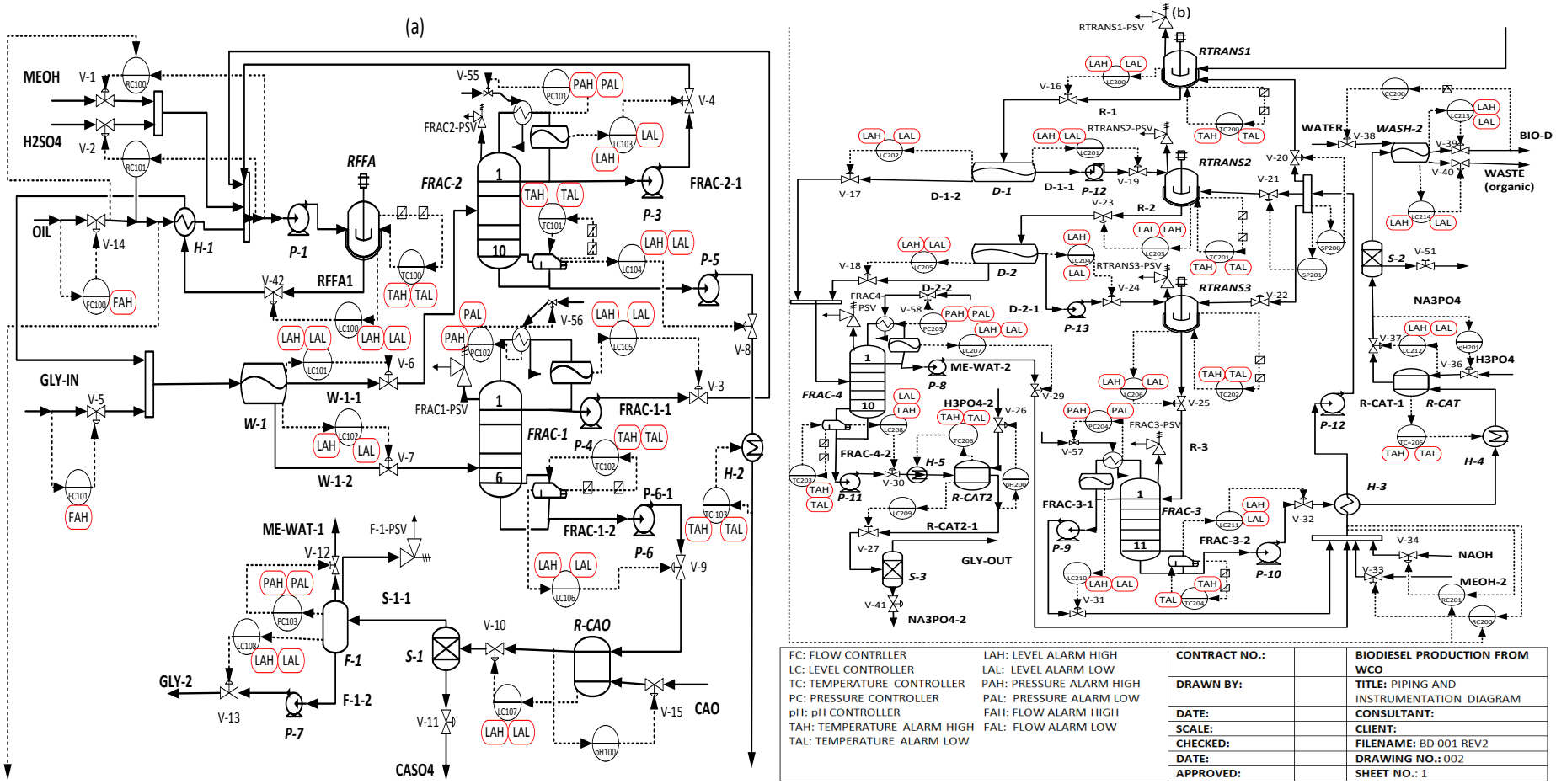

Figure 3.18 HAZOPed process diagram for biodiesel production from WCO: (a) esterification section (b) transesterification section.

This chapter discussed the development of two biodiesel processes, which are then optimized for multiple objectives to determine the better process. Processes are simulated realistically in Aspen Plus V8.0 and Aspen Plus Dynamics V8.0 using detailed reaction mechanism and detailed constituents of WCO. MOO is carried out using Excel based NSGA-II implemented in VBA. Several bi-objective optimization studies are conducted on the simulated process to determine the trade-off between conflicting objectives such as profit, heat duty and organic waste. Further, PWC system is developed for the chosen biodiesel process using IFSH methodology, the steps of which are discussed systematically in this chapter. This is a top-down systematic PWC method, which is proven to be effective in developing robust PWC for the various processes. However, its applicability to the complex multiunit biodiesel production from WCO process has been studied for the first time in this research. Also, the criteria for performance evaluation, applicable for PWC system evaluation, are presented.

Later, development of OTS for biodiesel process is discussed comprehensively. Dynamic model with control structure is developed in APD. Aspen OTS Framework is the used on top of APD. Various functionalities of OTS, including the partition mechanism, are also discussed thoroughly in this chapter. The developed OTS possesses several important characteristics of an effective OTS. Several scenarios, such as equipment malfunctions, fire, pressure safety valve, bursting disk, interlock and startup, which may occur in a real plant can be studied effectively using the developed OTS. At last, HAZOP analysis is carried out for this process. HAZOP report includes guide words, causes, consequences and recommendations for several potential scenarios. This simple HAZOP analysis is

meant to serve as a basis for the trainees to understanding the possible source of fault so that a proper action can be taken. Next chapter discusses the results obtained from the application of the methodologies discussed in this chapter to the biodiesel process.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, firstly, the results of detailed process simulation are discussed. The present study simulates the two process alternatives for biodiesel production from WCO considering detailed constituents of WCO and detailed kinetics (esterification and transesterification are represented by 10 and 96 kinetic reactions, respectively). Later, Pareto-optimal fronts obtained from MOO for different conflicting objectives, i.e. maximum profit, minimum heat duty and minimum organic waste, are discussed for both processes. NSGA-II is used to carry out MOO in this study. NSGA-II, implemented in Excel, is linked with biodiesel process model developed in Aspen Plus. A systematic comparison is carried out to find out the better process alternative. Effect of using detailed oil components versus a lumped component is also investigated. This analysis suggests the importance of using detailed constituents of WCO. Additionally, the quality of biodiesel is evaluated and compared against EN14214. Results show that the quality of produced biodiesel meets and exceeds the EN standards. Results of PWC structure resulted from the application of systematic IFSH are then presented and discussed for several disturbances.

Its performance is evaluated based on some advance performance evaluation criteria such as settling time of biodiesel production rate, deviation from the

production target (that affects economics) and total variation in manipulated variables (that depicts the control effort needed to stabilize the process). Also, dynamics of several process variables are shown for the considered disturbances. Finally, OTS results for different scenarios are presented and explained in rigor. These scenarios include equipment malfunctions, fire, pressure safety valve, bursting disk, interlock, and startup. To assist the trainees identify the possible source of faults to take appropriate action, a simple HAZOP analysis is also carried out.

4.2 Steady State Simulation Results

This work deals with development of the complete process in Aspen Plus. Steady state simulation results are validated against the data reported in the literature (see Table 4.1a and Table 4.1b). Initially, the process simulation results are validated against the literature data for the capacity considered in the respective source (see Table 4.1a). Then the capacity is increased to the present capacity of 120 kt/annum and compared against the data reported in several sources for the processes having different capacities (see Table 4.1b). Steady state values of important variables can be seen in Figure 3.3 and 3.3. Table 4.1 shows that the simulation results (product purity and conversion) are in agreement with the reported data. However, it should be noted that every paper referred to has different capacity as compared to the capacity considered in this work. This work develops a process keeping in mind the WCO availability in Malaysia. Parameters such as, methanol to oil ratio, constituents of oil, composition of constituents of oil, number of reaction, reaction kinetics etc are also different compared to what has been considered in this study, as mentioned in

previous sections. Also, there are differences in the process scheme such as, number of reactors used, sequence of unit operations etc. In addition, thermodynamics property used in the respective references is different that may lead to the different results.

Table 4.1a Validation of steady state simulation results for same capacity.

Parameters	**Biodiesel process 1 adopted from Sharma and Rangaiah (2013b)**	**Sharma and Rangaiah (2013b)**	**Biodiesel process 2 adopted from Morais et al. (2010)**	**Morais et al. (2010)**
Capacity	20 kt/annum	20 kt/annum	3.4 kt/annum	3.4 kt/annum
Thermo-physical property method	UNIF-DMD	UNIQUAC	UNIQUAC	UNIQUAC and NRTL
Type of oil	WCO	WCO	Pure oil	WCO
FFA content (wt%)	5	5	0	6
Lumped/ Detailed constituents	Detailed	Lumped	Lumped	Lumped
Esterification; transesterification reactor(s)	1;3	1; 3	0; 3	1;1
Intermediate phase separator in transesterification	Yes	Yes	Yes	No
Washing scheme	Methanol removal followed by washing	Methanol removal followed by washing	Washing followed by methanol removal	Washing followed by methanol removal
Mass flow & Purity of biodiesel(w/w %)	≈ 20 kt/annum & 99.2	≈ 20 kt/annum & >99	≈ 3.3 kt/annum & >99	≈ 3.3 kt/annum & 99.1
Purity of glycerol (w/w %)	96.3	>95	>99	91
Overall conversion (%)	99.5	>99	>99	≈ 99

Table 4.1b Validation of steady state simulation results and process comparison.

Parameters	**Present simulation: Biodiesel process 1**	**Present simulation: Biodiesel process 2**	**Sharma and Rangaiah (2013b)**	**Zhang et al. (2012)**	**Garcia et al. (2010)**
Capacity	120 kt/annum	120 kt/annum	20 kt/annum	200 kt/annum	73.5 kt/annum
Thermo-physical property method	UNIF-DMD	UNIF-DMD	UNIQUAC	UNIQUAC	NRTL and UNIQUAC
Type of oil	WCO	WCO	WCO	Pure oil	Palm, Soyabean, WCO
FFA content (wt%)	6	6	5	0	5
Lumped/ Detailed constituents	Detailed	Detailed	Lumped	Lumped	Detailed
Esterification; transesterification reactor(s)	1;3	1;3	1; 3	0; 3	1; 2
Intermediate phase separator in transesterification	Yes	No	Yes	Yes	No
Washing scheme	Methanol removal followed by washing	Washing followed by methanol removal	Methanol removal followed by washing	Methanol removal followed by washing	Washing followed by methanol removal
Purity of biodiesel(w/w %)	99.3	99.4	>99	>99	>98
Purity of glycerol (w/w %)	96.5	95.3	>95	>99	19.71
Overall conversion (%)	99.6	99.45	>99	>99	Up to 94

In addition, simulated results are also validated against real data provided by consultant (Mr. Chetan Sayankar, consultant for biodiesel and ethanol process, SRS biodiesel and engineering Pvt. Ltd.), and found to be reasonable. However, a complete plant design is not validated due the differences in the technology and also

confidentiality. Additionally, validation for several other parameters is also presented wherever required, for example fixed capital investment, settling time, DPT etc.

4.3 Multi-objective Optimization (MOO) of Biodiesel Processes

MOO is carried out using NSGA-II to determine the optimal solutions between conflicting objectives. Two bi-objective problems, namely profit vs heat duty and profit vs organic waste, are considered for each process. Analysis in terms of these objectives is important as these indicate the vital economic and environmental aspects of the process. The resulted Pareto-optimal fronts are then discussed as given below. Trends of decision variables with respect to profit are presented. These trends are subjected to many constraints as mentioned in Chapter 3. One optimal solution from each process is then considered and compared for further discussion where a comparison is conducted to determine the best process alternative. The comparison is conducted based on capital investment, methanol requirement, biodiesel product quantity, manufacturing cost, organic waste formation, heat duty requirement and profit. Also, the quality of biodiesel product is compared against EN standard for the same optimal solution.

4.3.1 Pareto-optimal Solutions for Process 1

Two cases, namely profit vs heat duty and profit vs organic waste are investigated for process 1. Pareto-optimal front between the objectives and trends of decision variables vs profit are presented below for each case.

(a) Case 1: Trade-off between profit and heat duty

The trade-off between profit and heat duty for Process 1 is shown in Figure 4.1a. All the solutions on the Pareto-optimal front are equally good for the objectives used, and any solution can be selected based on engineer's preference and other requirements. The increase in annual profit from 47.45 to 55.44 million USD requires a proportional increase in heat duty from 10.20 to 11.75 MW (Figure 4.1a).

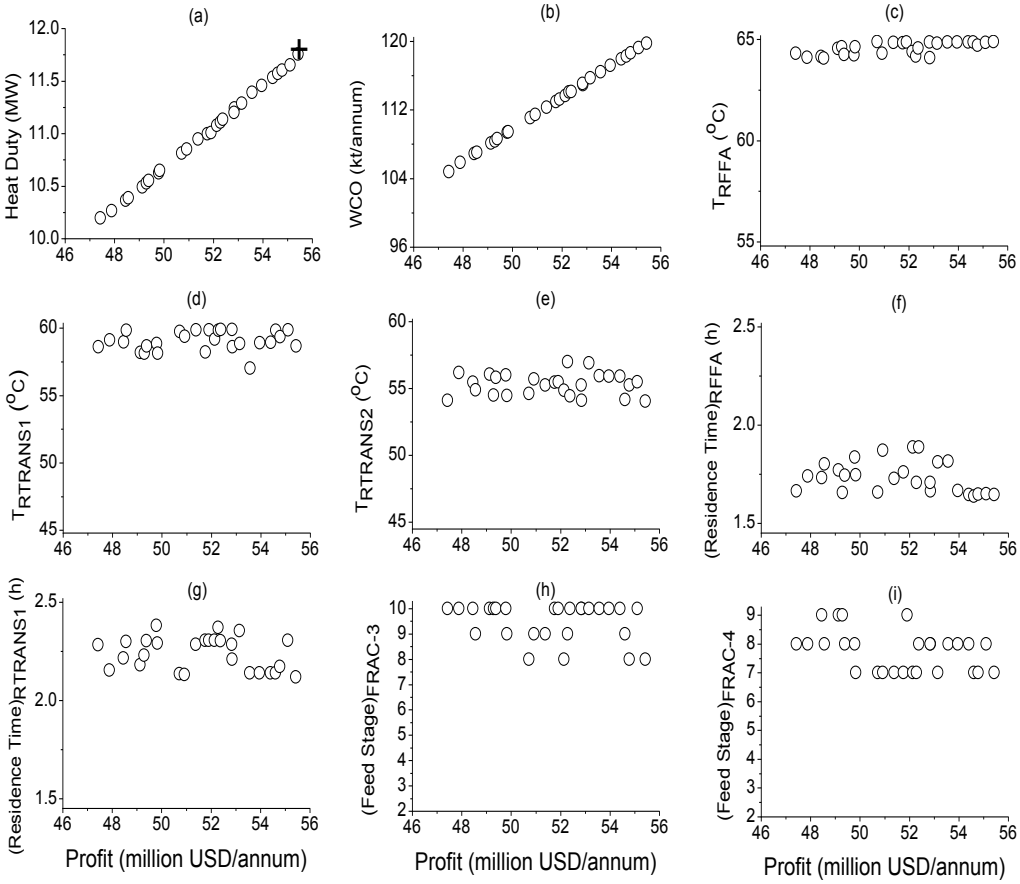

Figure 4.1 Simultaneous maximization of profit and minimization of heat duty for Process 1.

This is mainly due to the increased WCO from 104.76 to 119.73 kt/annum (Figure 4.1b). The temperatures of esterification reactor 'T_{RFFA}' (Figure 4.1c), transesterification reactor '$T_{RTRANS1}$' (Figure 4.1d) and transesterification reactor '$T_{RTRANS3}$' (not shown in Figure 4.1 for brevity; see Figure A.1 in the Appendix A) stay near to their upper bounds. Further, $T_{RTRANS2}$ (Figure 4.1e) varies around 55^{o}C. These higher reactor temperatures lead to better conversion and consequently higher profit. However, this increases the size and so cost of phase-separators 'W-1', 'D-1' and 'D-2' resulting in higher FCI. Optimal residence time in esterification reactor '$(\text{Residence Time})_{RFFA}$' (Figure 4.1f) is largely scattered between 1.6 to 1.9 h. This suggests that smaller reactor volume i.e. smaller residence time (1.6 to 1.9 h) with higher temperature is sufficient to achieve the required conversion of the FFAs to biodiesel. Optimal residence times in transesterification reactors: '$(\text{Residence Time})_{RTRANS1}$' (Figure 4.1g), '$(\text{Residence Time})_{RTRANS2}$' (Figure A.1b in the Appendix A) and '$(\text{Residence Time})_{RTRANS3}$' (Figure A.1c) are largely scattered near to their upper bounds. These are required to obtain optimum conversion of WCO, though larger reactor volumes increase the capital cost. In general, optimum feed stages for columns 'FRAC-1' (Figure A.1d), 'FRAC-2' (Figure A.1e), 'FRAC-3' (Figure 4.1h) and 'FRAC-4' (Figure 4.1i) are scattered towards their upper bounds. These do not have much impact on FCI, but increases the profit by reducing the utility cost for the column reboiler and condenser. Pareto-optimal solution (shown as + in Figure 4.1a) is considered for further discussion in the section 4.3.3. Table A.3 in the Appendix A presents the key data of selected streams corresponding to this optimal solution.

(b) Case 2: Trade-off between profit and organic waste

Figure 4.2a presents Pareto-optimal front obtained for maximizing profit and minimizing organic waste. Organic waste increases from 0.183 to 0.202 kt/annum for the profit improvement from 48.32 to 55.68 million USD per annum. Methanol, glycerol, tri/di/mono-glycerides, FFAs and FAMEs are the constituents of organic waste. As the waste stream ('WASTE' in Figure 3.3) contains glycerol and FAME, minimization of organic waste improves the profit to some extent. In general, the main decision variable affecting the profit and organic waste is the amount of WCO processed (Figure 4.2). Higher values of T_{RFFA}, $T_{RTRANS1}$, $T_{RTRANS3}$ (Figure 4.2b-4.2e) also improve the profit as larger amount of biodiesel is produced from WCO in smaller reactors at higher temperatures. As $T_{RTRANS2}$ stays near to its lower bound of 45^{o}C (Figure A.2a in the Appendix A), higher temperature is required in $T_{RTRANS3}$ to convert the remaining oil to FAME (Figure 4.2e). Lower $T_{RTRANS2}$ favors the profit by reducing the cost of phase separator 'D-2'. As higher temperatures of reactors favor both objectives similarly, most of the decision variables related to the temperature are closer to their upper bounds. However, this leads to increase in FCI as larger phase separators are required to achieve sufficient separation.

Optimal residence time of esterification reactor: '$(\text{Residence Time})_{RFFA}$' (Figure 4.2f) is largely scattered between 1.5 to 1.88 h, which suggests that smaller reactor operating at higher temperature is better to achieve the required conversion of FFAs to FAME. Optimal residence times of first two transesterification reactors are largely scattered towards their upper bounds (Figures A.2b and A.2c); $(\text{Residence Time})_{RTRANS3}$ (Figure 4.2g) is scattered between 1.6 to 1.93 h.

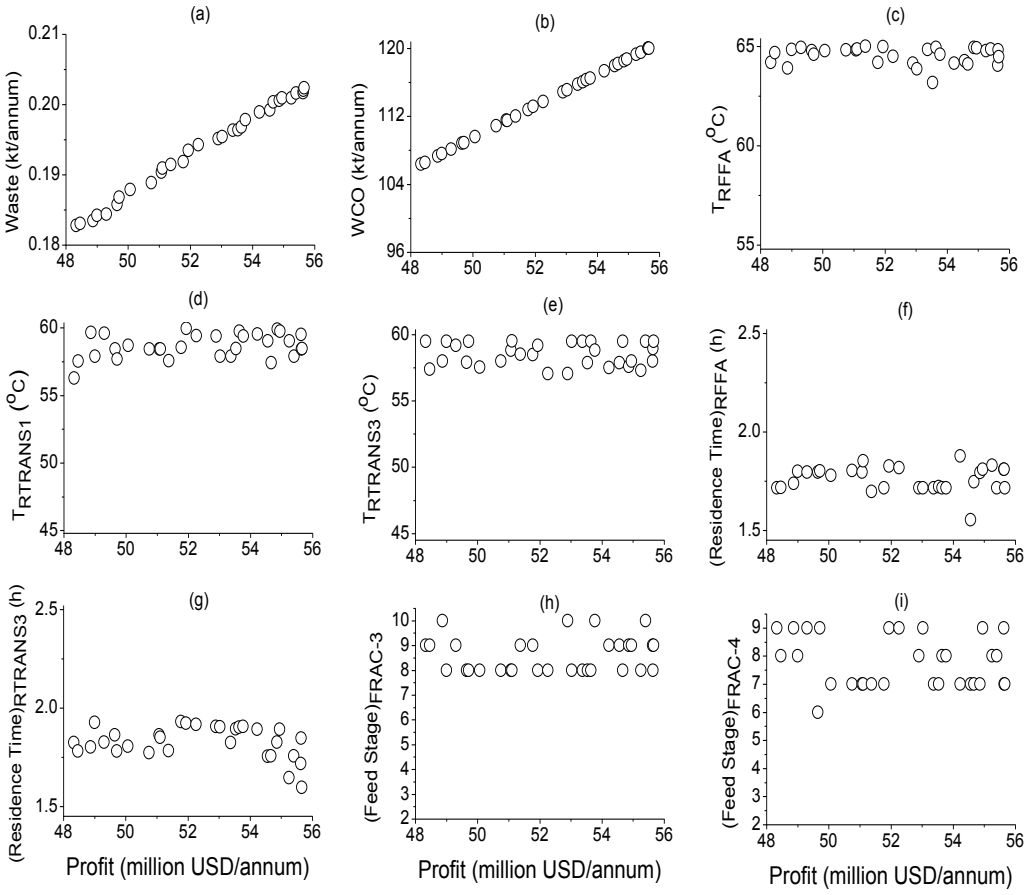

Figure 4.2 Simultaneous maximization of profit and minimization of organic waste for Process 1.

These are required to obtain optimum conversion of WCO to FAME, which increases the profit and also reduces amount of organic waste. The optimum feed stages for columns 'FRAC-1' (Figure A.2d), 'FRAC-2' (Figure S2e), 'FRAC-3' (Figure 4.2h) and 'FRAC-4' (Figure 4.2i) are scattered towards their upper bounds, which are the stages close to the reboiler. Although these do not affect the generation of organic waste, they increase the profit by reducing the energy requirements of the columns.

4.3.2 Pareto-optimal Solutions for Process 2

Similar to MOO study for process 1, two cases namely profit vs heat duty and profit vs organic waste, are investigated for process 2. Pareto-optimal front between the conflicting objectives and trends of decision variables vs profit are presented below for each case.

(a) Case 1: Trade-off between profit and heat duty

The trade-off between profit and heat duty for Process 2 in Figure 4.3a is similar to that for Process 1. The profit improves from 44.30 to 54.57 million USD per annum as heat duty increases proportionately from 13.71 to 16.36 MW. As opposed to Process 1, Process 2 has no intermediate phase separators, whose cost would vary as a result of variation in the reactor temperature. In both the processes, larger profit can obtained at higher capacity, but this also increases the heat duty. As expected, increase in heat duty and profit (Figure 4.3a) is mainly due to the increased WCO from 97.13 to 118.02 kt/annum (Figure 4.3b). Initially, esterification reactor temperature, 'T_{RFFA}' (Figure 4.3c) stays near to its upper bound. Later, it is scattered between 61.9 to 65^{o}C (Figure 4.3c). Transesterification reactor temperature, 'T_{RTRANS}' is scattered between 52 to 60^{o}C, especially in the later part (Figure 4.3d). Higher profit is obtained as better conversion of WCO to FAME is achieved at higher temperatures. The residence time of esterification reactor '(Residence Time)$_{RFFA}$' increases from 1.54 to 2.5 h, particularly at high profit (Figure 4.3e). This is required to obtain sufficient conversion of FFAs to FAME.

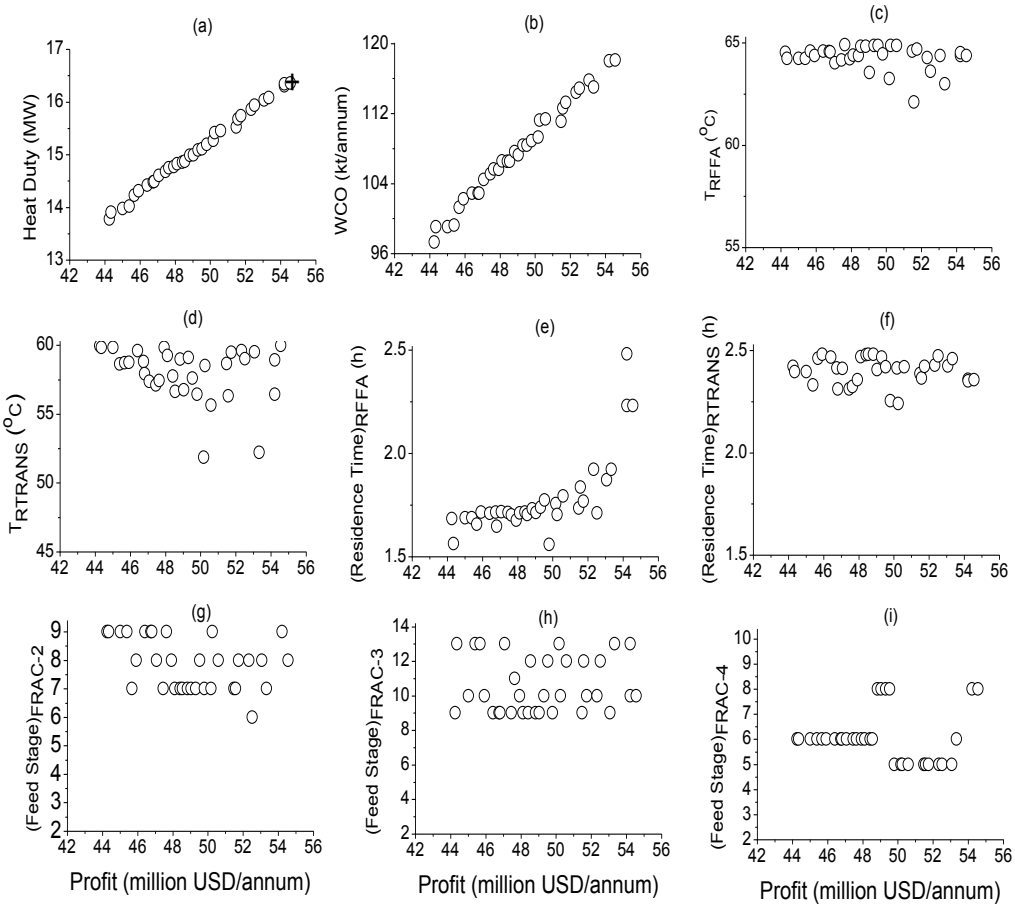

Figure 4.3 Simultaneous maximization of profit and minimization of heat duty for Process 2.

Optimal residence time of transesterification reactor '(Residence Time)$_{RTRANS}$' (Figure 4.3f) is scattered between 2.24 to 2.5 h. Capital cost increases with reactor size, but large reactor is required to obtain optimum conversion of WCO. Transesterification reactor design is very critical as this process has only one reactor unlike in Process 1, which has three transesterification reactors in series. In general, optimum feed stages for columns 'FRAC-1' (Figure A.3 in the Appendix A), 'FRAC-2' (Figure 4.3g), 'FRAC-3' (Figure 4.3h) and 'FRAC-4' (Figure 4.3i) are scattered towards their upper bounds, which increase the profit by reducing the

utility cost in reboilers and condensers. The optimal solution, shown as + in Figure 4.3a, is taken for further analysis in section 4.3.3. Table A.4 in the Appendix A presents the key data of selected streams corresponding to this optimal solution.

(b) Case 2: Trade-off between profit and organic waste

Figure 4.4a presents the Pareto-optimal solutions obtained for simultaneous maximization of profit and minimization of organic waste for Process 2. Organic waste increases from 0.253 to 0.295 kt/annum for the improvement in profit from 44.15 to 54.50 million USD per annum. These increases are mainly due to the increased WCO from 98.98 to 118.35 kt/annum (Figure 4.4b). Note that only methanol in streams: 'ME-WAT-1', 'ME-WAT-2' and 'ME-WAT-3' in Figure 3.4, is the organic waste in Process 2, which does not affect profit much. Optimal values of T_{RFFA} and T_{RTRANS} are near to their upper bounds of 65 and 60^{o}C, respectively (Figures 4.4c and 4.4d), which improve the profit by maximizing the product formation. Optimal $(\text{Residence Time})_{RFFA}$ increases from 1.55 to 2.23 h, which is required to convert FFAs into FAME (Figure 4.4e). Optimal $(\text{Residence Time})_{RTRANS}$ is near to its upper bound (scattered between 2.32 to 2.5 h), for converting most of the oil into FAME (Figure 4.4e); this has favorable impact on the profit without affecting the organic waste. Optimum feed stages for columns 'FRAC-1' (Figure A.4 in the Appendix), 'FRAC-2' (Figure 4.4g), 'FRAC-3' (Figure 4.4h) and 'FRAC-4' (Figure 4.4i) are scattered towards their upper bounds, which increase the profit by reducing the utility cost in reboilers and condensers of different columns. Similar to Process 1, they do not affect the generation of organic waste but improve the profit by reducing COM.

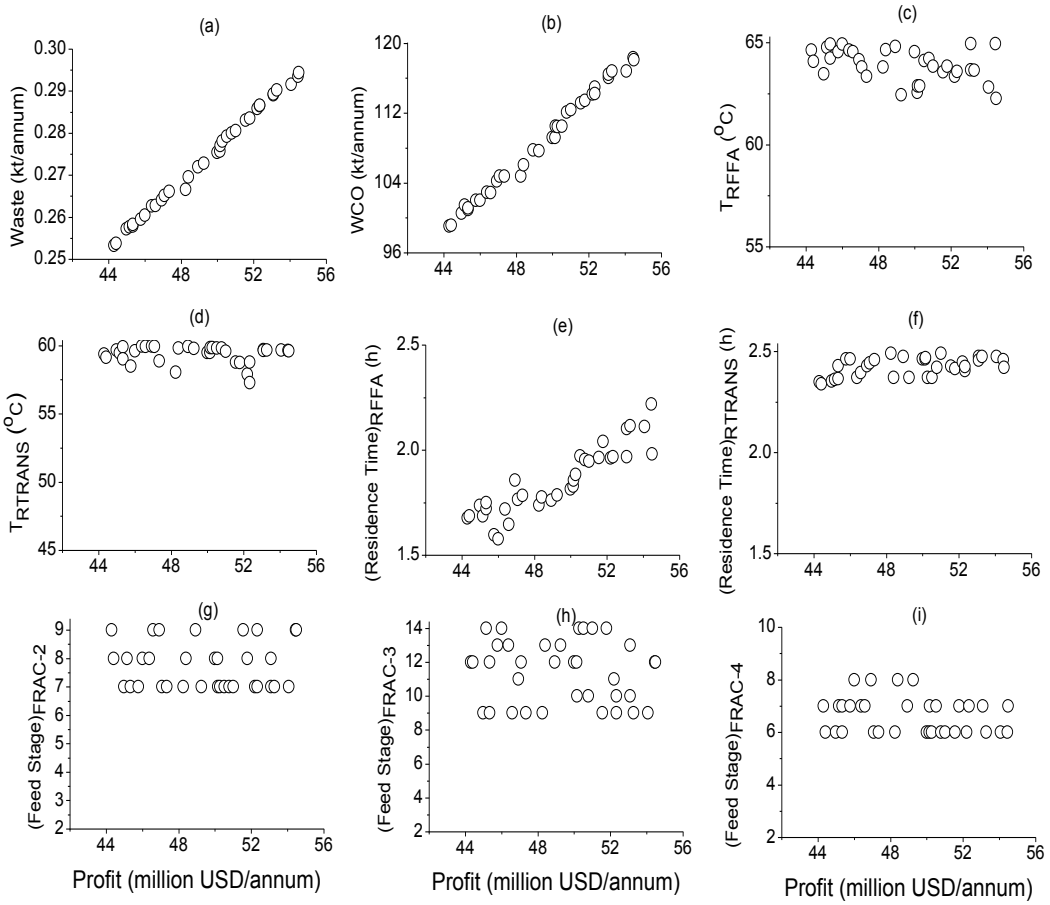

Figure 4.4 Simultaneous maximization of profit and minimization of organic waste for Process 2.

4.3.3 Comparison of Processes 1 and 2 for their Economic Merit and Environmental Impact

Table 4.2 compares several quantities for the selected optimal solutions for Processes 1 and 2 (represented by + in Figure 4.1a and Figure 4.3a, respectively). Although all the solutions on the Pareto-optimal front are equally good, the optimal solution corresponding to the highest profit for each process is chosen for a fair comparison.

Table 4.2 Comparison of Processes 1 and 2 (corresponding to the optimal solution + in Figures 4.1a and 4.3a).

Quantity	Process 1	Process 2	% Difference
	A	**B**	**[A-B]×100/A**
FCI or C_{GR} (million USD)	12.95	12.73	1.70
COM (million USD/annum)	73.5	72.8	0.95
Revenue (million USD/annum)	129	127	1.6
Profit (million USD/annum)	55.44	54.57	1.57
Methanol flow rate (kt/annum)	14.12	13.76	2.55
Biodiesel produced (kt/annum)	121.09	118.95	1.77
Organic waste (kt/annum)	0.221	0.292	-32.13
Heat Duty (MW)	11.75	16.36	-39.23
Optimal DVs			
Optimum T_{RFFA} (^oC)	65	65	
Optimum $T_{RTRANS1}$ (^oC)	60	60	
Optimum $T_{RTRANS2}$ (^oC)	55	-	
Optimum $T_{RTRANS3}$ (^oC)	60	-	
Optimum (Residence time)$_{TRFFA}$ (h)	1.7	2.5	
Optimum (Residence time)$_{TRTRANS1}$ (h)	2.1	2.3	
Optimum (Residence time)$_{TRTRANS2}$ (h)	2.1	-	
Optimum (Residence time)$_{TRTRANS3}$ (h)	2.1	-	
Optimum (Feed Stage)$_{FRAC-1}$	5	3	
Optimum (Feed Stage)$_{FRAC-2}$	7	8	
Optimum (Feed Stage)$_{FRAC-3}$	8	10	
Optimum (Feed Stage)$_{FRAC-4}$	7	8	

West et al. (2008) reported C_{TM} of 1.1 million USD (when CEPCI = 394) for a biodiesel plant of capacity 8 kt/annum with WCO as the feedstock. Further, Sharma and Rangaiah (2013b) reported C_{TM} of 2.88 million USD (for CPECI = 600) for a biodiesel plant of capacity 20 kt/annum with WCO as the feedstock.

Projected C_{TM} for a plant capacity of 120 kt/annum, using the six-tenths rule (Sieder et al., 2010), and CEPCI of 600, is 8.44 million USD (based on Sharma and Rangaiah, 2013b) and 8.5 million USD (based on West et al., 2008). In the present study, C_{TM} of 9.31 million USD for Process 1 and 9.30 million USD for Process 2 are obtained, and these are consistent with the previous studies. The small increase in C_{TM} is mainly due to the increased number of processing steps in both the processes (see Figures 3.1 and 3.2 in Chapter 3).

From Table 4.2, it can be noticed that FCI for Process 1 is slightly higher than that for Process 2, mainly due to the more number of equipments e.g. 3 transesterification reactors) involved in the former process. Amount of methanol required in Process 1 is slightly higher than that of Process 2, mainly due to slightly larger WCO and more methanol to oil ratio (required to maintain 6:1 methanol to oil ratio in each transesterification reactor) in Process 1 as some methanol is removed from the intermediate phase separators. As water wash column is placed after methanol recovery column in Process 1, recovered methanol is almost free from water. This leads to less energy-intensive methanol recovery. COM for Process 1 is marginally higher than that of Process 2, mainly due to higher FCI, labor cost and cost of chemicals in Process 1. Amount of organic waste generated in Process 1 is significantly lower (32%) than that in Process 2.

Also, heat duty of Process 1 is significantly lower (39%) than that of Process 2. Lower heat duty and lower organic waste suggest that Process 1 has lower environmental impact compared to Process 2. Lower heat duty indicates the lower energy demand, and lower environmental impact such as water pollution arising from disposal of organic waste in the water bodies. The menace due to such disposal include the threat to the animal kind, especially aquatic life due to the depletion of dissolved oxygen (DO). DO depletion can occur due to the increased biological oxygen demand and prevention of sunlight from entering into the water bodies because of the formation of the thin film of oily liquid on top of the water surface.

Further, the present study reveals that, despite more number of equipments involved, Process 1 is slightly more profitable than Process 2. This is mainly due to reduced utility cost and increased revenue resulting from the increased product formation (Table 4.2); these in turn are attributed to the processing sequence with three CSTRs in series, where intermediate phase separators are used to remove heavy phase and prevent backward reactions. Moreover, in Process 1, biodiesel and glycerol are separated first followed by methanol separation and washing of biodiesel. The advantages of this scheme include: (1) it prevents backward reactions as methanol is not removed until separation between biodiesel and glycerol is complete, and (2) as water washing is carried out after methanol removal, the recovered methanol contains very small fraction of water, which avoids energy intensive methanol-water separation and enables methanol re-use in the process. Comparative results in Table 4.2 for the optimized process alternatives are consistent with Myint and El-Halwagi (2009). Myint and El-Halwagi (2009) concluded that the

best flow-sheet is with the biodiesel and glycerol separation first, followed by methanol recovery and finally water washing.

4.3.4 Effect of detailed versus lumped components and quality

Properties of biodiesel obtained from Aspen Plus simulation, are analyzed to evaluate the quality of biodiesel, and then it is compared against EN standards (European Norms: European standards that describe the requirements and test methods for biodiesel). The results presented in Table 4.3 show that the quality of the produced biodiesel meets the minimum required standards. To investigate the effect of using detailed composition of oil versus lumped component, optimized Process 1 was simulated with all triglycerides lumped into triolein and all FFAs lumped into oleic acid.

Total heating load (Q_H), which is the sum of heating required in reboilers, reactors and heaters, is compared for these two cases. It is found to be 5.61 MW when detailed oil components are used, compared to Q_H of 5.71 MW when the oil components are lumped together. The quality of biodiesel is also analyzed for these two cases. As expected, the constituent methyl esters considering detailed and lumped oil components are different; consequently, quality of the biodiesel is different (Table 4.3). This difference arises due to the different properties (critical temperature, accentric factor, boiling point etc.) of different glycerides that are not considered when using the a single lumped component. The differences in the results indicate that more details, as used in this study, should be considered for more realistic simulation and optimization.

Table 4.3 Comparison of biodiesel quality for the optimal solutions of Processes 1 and 2 (shown as + in Figures 4.1a and 4.3a) with those required by EN.

Parameters	**Process 1 (Detailed components)**	**Process 1 (Lumped component)**	**Process 2 (Detailed components)**	**EN14214 Palmoilworld (2013)**
Methyl-O [wt%]	38.01	99.12	36.72	-
Methyl-P [wt%]	48.79	0.0	47.59	-
Methyl-M [wt%]	2.10	0.0	3.20	-
Methyl-S [wt%]	2.70	0.0	3.79	-
Methyl-Li [wt%]	7.69	0.0	8.20	-
Biodiesel (= sum of above)[wt%]	99.29	99.12	99.5	> 96.5
Monoglycerides [ppm]	286	292	251	< 8000
Diglycerides [ppm]	99	103	83	< 2000
Triglycerides [ppm]	112	115	99	< 2000
Glycerol [ppm]	Trace	Trace	Trace	< 2500
Methanol [ppm]	608	539	316	< 2000
Density (15°C) [kg/m^3]	869.42	861.63	866. 167	860-900

4.4 Performance Assessment of the Plantwide Control (PWC) System for Process 1

In the previous section, two processes are optimized and compared considering profit, heat duty and organic waste as the objectives. The better process is then identified based on several criteria such as FCI, methanol requirement, biodiesel produced, COM, organic waste formation, heat duty and profit. Later, a suitable PWC system is developed for the chosen process i.e. process 1. The final control system for the complete biodiesel plant consists of 52 control loops (Figure 3.9 in Chapter 3). The details of CV-MV pairings, reasons for pairings and tuning parameters are presented in Table 3.4 of Chapter 3. This control structure cannot be compared directly with the previous studies (Shen et al., 2011; Cheng et al., 2014) on control of biodiesel process as they use different production processes. However, the main difference in the control structure besides inventory loops is quality controllers, i.e. FFA and triglyceride impurity, which decide remote set point to the ratio controllers 'RC100' & 'RC200' respectively, and methanol impurity in biodiesel product by manipulating the water flow rate.

Previous studies (Shen et al., 2011; Zhang et al., 2012) on PWC of biodiesel production use pure vegetable oil, which does not require the esterification section, needed when using WCO as feedstock, to convert FFAs into biodiesel. Therefore, the resulted control structure in the present work is different (i.e., controllers in top/esterification section, and temperature controllers for RTRANS1, RTRANS2, RTRANS3 and H-4, in Figure 3.9). In this work, we included temperature controllers for CSTRs as the temperature is found to be varying. Other control loops in the

transesterification section are similar to those presented in Zhang et al. (2012). Also, components and kinetics used in the present work are more detailed in terms of more number of reactions and detailed constituents of the WCO compared to those used in earlier studies (Shen et al., 2011; Zhang et al., 2012). This is required to obtain more realistic results. The effects, such as quality and heat duty, of using detailed constituents of WCO with detailed kinetics are depicted the previous section.

4.4.1 Transient Profile of Biodiesel Production Rate

Figure 4.5 depicts the transient profile of biodiesel production rate for the disturbances D1, D2, D6 and D7 explained in Table 3.3 of Chapter 3. It can be seen that the plant settles down smoothly to a new throughput after some time. By and large, the change in WCO produces a proportionate change in the biodiesel production rate.

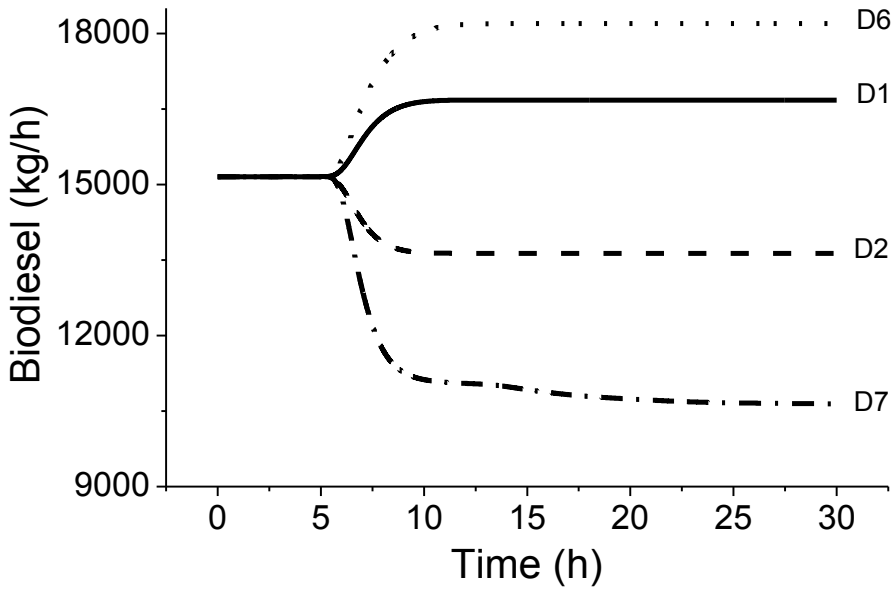

Figure 4.5 Transient profile of biodiesel production rate in the presence of selected disturbances.

Initially, the plant is run for 5 h, after which the disturbances are introduced, one at a time. It is clear from the figure that the developed PWC system is able to control the process for reasonably large disturbances too i.e. +20% and -30% change in WCO. Transient responses are smooth and stable. Expectedly, D7 requires more settling time as compared to other disturbances as a result of larger throughput change, whereas D1 and D2 require relatively less setlling time.

4.4.2 Performance of the PWC System Based on Performance Criteria

The performance of the designed control system is assessed for the disturbances D1 to D7. Due to the large number of controllers, it is extremely difficult to analyze the performance of each and every control loop (say, in terms of integral square error). Also, the PWC system performance should be evaluated from a plantwide perspective. The criteria for the assessment of control system's performance should be effective and easy, and they should describe several factors such as an economic index and smoothness. Vasudevan and Rangaiah (2010) proposed several criteria for the performance evaluation of PWC systems. Some of these, viz settling time (indicative of smooth and safe operation of the plant), DPT (denotes an indirect economic index) and overall TV (indicator of the control efforts required for PWC structure to attain stable operation) are used for the performance quantification.

Table 4.4 presents the performance of the control system (i.e comprising all control loops) for the disturbances D1 to D7. For the complete biodiesel plant, having a capacity of 120 kt/annum, the observed settling time of the biodiesel

production rate in the presence of disturbances D1 to D6 is reasonable compared to the settling time of less than 10 h for a biodiesel plant processing 10 kmol/h of oil (i.e. nearly 71 kt/annum) (Shen et al., 2011). Larger settling time of about 14.2 h is observed for the relatively large disturbance D7 (-30% in the WCO). This settling time is required for the PWC system due to the more time required in phase separators and the larger holdup in reactors. DPT is the smallest for disturbance D3, wherein -10% change is introduced in the pre-exponential factor of reactions converting WCO to biodiesel. DPT for the disturbances D1 to D5 is comparable (Table 4.4). As expected, DPT is the largest for D7, followed by D6 due to the magnitude of change in WCO. In general, increase in the magnitude of change in throughput leads to the increase in DPT. Note that smaller DPT is desired, which denotes that the PWC system is efficient in achieving the new production rate target, and so the economic loss is smaller.

Table 4.4 Performance of the PWC system designed for the complete biodiesel process.

No.	**Performance Criterion**		
	Settling time (h)	**DPT (kg)**	**Overall TV**
D1	6.4	2123	445
D2	6.3	2042	429
D3	2.2	318	63
D4	7.4	2223	446
D5	7.2	2133	439
D6	8.7	4073	649
D7	13.2	7556	1104

Similar to DPT results, D3 has the least overall TV, whereas D7 has the largest. As in case of DPT, the increased magnitude of change in throughput leads to increased overall TV (i.e., increased control effort).

4.4.3 Waste Cooking Oil (WCO) Accumulation due to the Disturbances

The accumulation of WCO in the presence of disturbances D1, D2, D6 and D7 is illustrated in Figure 4.6. For brevity, the accumulation of only WCO is shown in the figure. However, the accumulation of all components in the complete plant as well as in individual unit operations can be monitored to see if any inventory loop needs to be modified. Figure 4.6 shows that the accumulation is more for larger throughput changes.

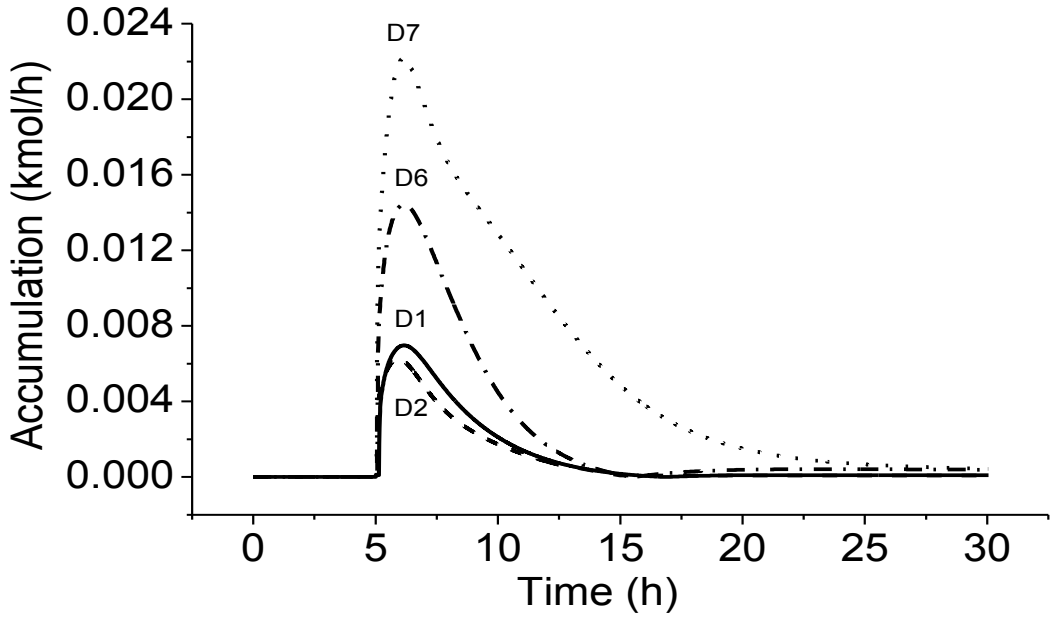

Figure 4.6 WCO accumulation due to disturbances D1, D2, D6 and D7 explained in Chapter 3.

This is due to the more control efforts that are needed to stabilize the process. Accumulation of WCO for all disturbances eventually reaches to zero, which is important for safe and stable operation of the plant. Accumulation for D7 (i.e. for -30% change in WCO) is highest and requires more time (around 20 h) to settle down to zero. This is followed by D6 (around 15 h), D1 (around 14 h) and D2 (around 14 h).

4.4.4 Profiles of Purity and Impurity

Profiles of TG impurity in biodiesel, methanol impurity in biodiesel and biodiesel purity (i.e. wt% of biodiesel in the product) due to the selected disturbances are depicted in Figure 4.7. Both TG and methanol impurities are observed to be below their permissible limit (i.e. TG impurity < 0.2 wt% and methanol < 0.2 wt%) as per the EN standards (Palmoilworld, 2014). This proves that the proposed control system is effective in maintaining the product quality. A small increase in TG impurity is observed in Figure 4.7 for the increased flow rate of WCO (for D1 and D6) and vice a versa (for D5 and D7). A similar trend is observed for FFA and methanol impurity. Consequently, a reverse trend is observed for biodiesel purity, but it is also kept under control (i.e. > 96.5 wt%) for all disturbances. This reverse trend is due to the changes in the composition of other components of the stream 'BIO-D'. For example, if a stream has two componets A and B and if the mass fraction of A increases, the mass fraction of B will decrease.

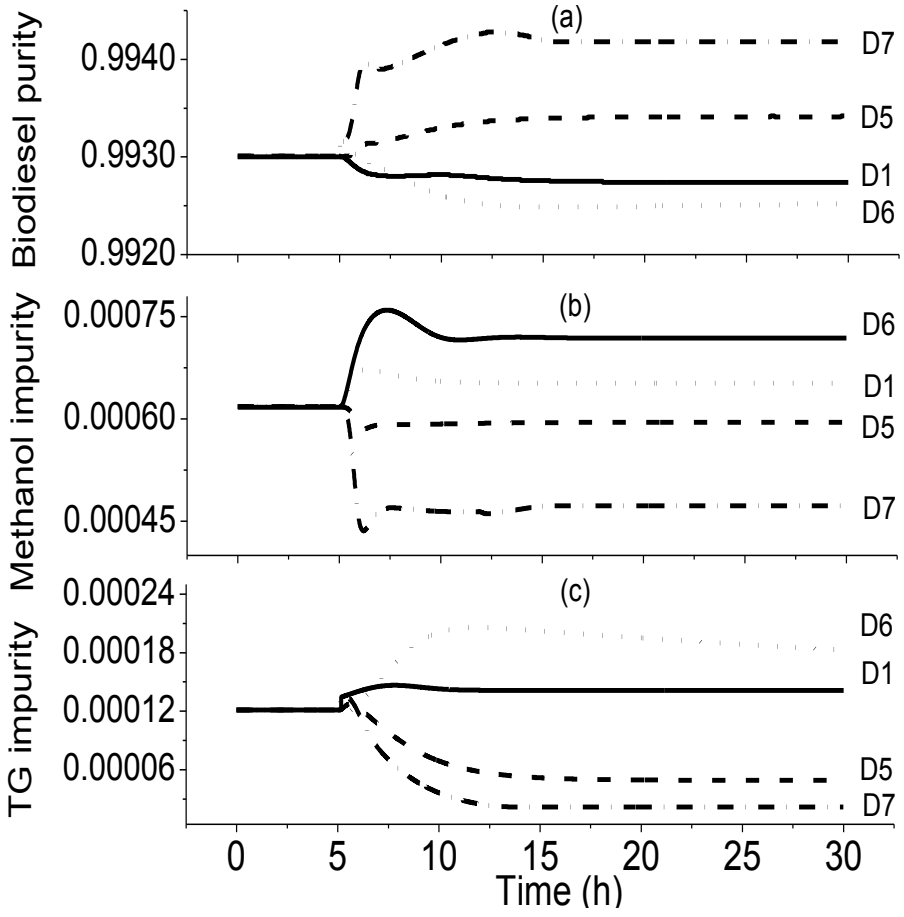

Figure 4.7 Profiles of TG impurity (wt %) in biodiesel, methanol impurity (wt %) in biodiesel and biodiesel purity (wt % of biodiesel) in the presence of selected disturbances explained in Chapter 3.

Table 4.5 compares biodiesel quality for the largest disturbances D6 and D7 (after reaching the steady state), against EN standards. Only D6 and D7 are studied here as if the quality of the biodiesel is maintained for these largest disturbances, quality of the biodesel will automatically be met for all other smaller disturbances too. This shows that the quality has been maintained despite such large disturbances. Note that these variables are not returning to their original values as there is no direct control of them. The respective controller would become active and maintain TG and

methanol impurity below their permissible limit as and when the variables violate the permissible limit. Recall that methanol ratio is manipulated to maintain TG impurity in biodiesel, and wash water flow rate is manipulated to maintain methanol impurity in biodiesel.

Table 4.5 Biodiesel quality for D6 and D7 against EN14214 standard.

Parameters	**D6**	**D7**	**EN14214** (MPOB, 2013)
Biodiesel [wt%]	99.18	99.39	> 96.5
Monoglycerides [wt%]	0.026	0.022	< 0.8
Diglycerides [wt%]	0.01	0.009	< 0.2
Triglycerides [wt%]	0.018	0.003	< 0.2
Glycerol [wt%]	0.0014	0.0012	< 0.25
Methanol [wt%]	0.064	0.044	< 0.2
Density (15°C) [kg/m^3]	881.6	878.51	860-900

4.4.5 Performance of Important Control Loops for Selected Disturbances

Figure 4.8 shows the performance of important control loops for selected disturbances. Other control loops (not shown for brevity) are also found to work equally well as those presented in Figure 4.8. Please refer to Figure 3.3 in Chapter 3 for the process operations such as 'RFFA'.

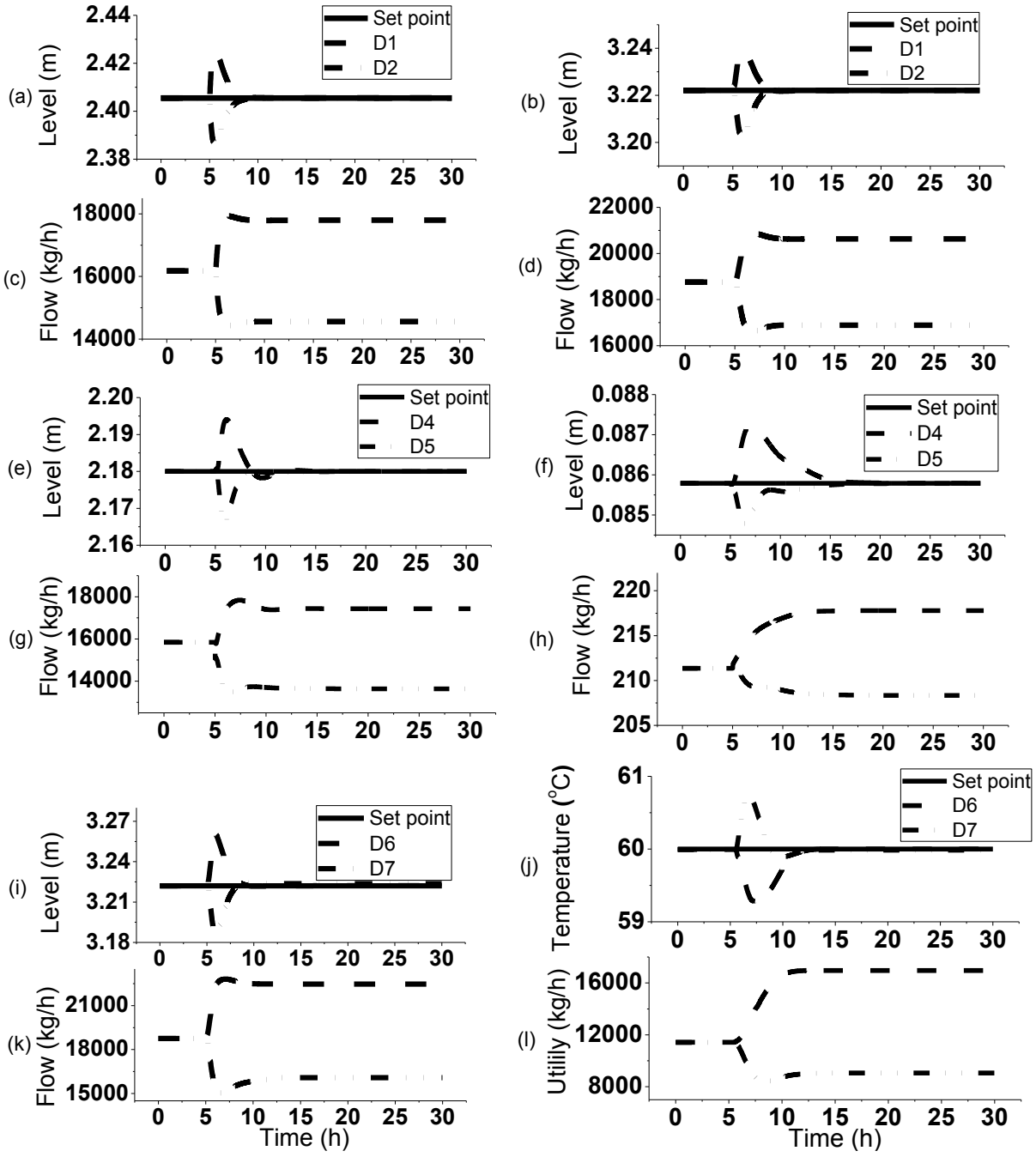

Figure 4.8 Performance of important loops for selected disturbances: (a) LC in 'RFFA', (b) LC in 'RTRANS1', (c) Flow from 'RFFA', , (d) Flow from 'RTRANS1', (e) First phase LC in 'WASH-2', (f) Second phase LC in 'WASH-2', (g) First flow from 'WASH-2', (h) Second flow from 'WASH-2', (i) LC in 'RTRANS2', (j) TC in 'RTRANS1', (k) Flow from 'RTRANS2', and (l) Utility flow in 'RTRANS1' (Note: LC- level control, TC- temperature control).

Due to the large number of control loops present in this PWC scheme, individual control loops are not assessed in terms of conventional time domain performance specification such as overshoot, rise time and integral error indices. Instead, as discussed above, comprehensive PWC performance assessment criteria are used. In any case, performance of important control loops in terms of overshoot and rise time can be seen in Figure 4.8. As the control loops are able to maintain the controlled variables at their respective set points for the disturbances tested, it can be inferred that the control loops are properly paired and tuned. Settling time of the control loops shown in Figure 4.8, including the level controllers in phase separators and reactor, justifies the overall settling time of biodiesel product given in Table 4.4. The observed settling time in the reactors is due to the larger holdup. Overall, control loops in the developed PWC system are performing satisfactorily in the presence of several disturbances.

4.5 Operator Training Simulator (OTS) for Process 1

The industrial processes are becoming extremely complex as a result of intense energy and material integrations. Ayral and De Jonge (2013) estimated the total annualized benefits from an OTS for a 100,000 bpd refinery to be 4.9 million dollars. These show the importance of OTS in the process industry. Several scenarios such as startup, interlock, equipment malfunctions, fire, pressure safety valve and bursting disk in the biodiesel plant, are studied using the developed OTS in APD and Aspen OTS Framework. Seborg et al. (2010) reported the typical failure rates of selected process components in the year 1986. Failure frequency in a year of control

valve, valve positioner, transducer, pressure measurement, orifice plate and D/P transmitter, magnetic flowmeter, thermocouple, mercury in a steel bulb, controller, pressure switch, and gas-liquid chromatography is reported to be 0.6, 0.44, 0.49, 1.14, 1.73, 2.18, 0.52, 0.027, 0.29, 0.14 and 30.6, respectively. Therefore, scenarios depicting the failure of process components should also be studied by operators as such failure/malfunctions can cause the process operation to enter an unacceptable region. These are presented and discussed from the perspective of operator training, in the following sub-sections. In addition to above scenarios, OTS lets trainees tune various PID controllers in real-time and increased time. It lets trainees try different setpoints, change auto/manual modes, drive the PIDs unstable with aggressive/robust tuning, and hence it lets trainees achieve proficiency in controller tuning thereby. Typically, OTS consists of two major components i.e. dynamic simulation of the process and control architecture. The focus of this work is on the development of the former.

4.5.1 Startup of Distillation Column 'FRAC-3'

Startup of unit operations is of vital importance for a quick, safe, smooth and economical operation. Figure 4.9 presents the startup of FRAC3 (i.e., the distillation column separating biodiesel from methanol in the transesterification section). To illustrate the effect of different startup schemes that could be adopted by trainee operators, two startup approaches, namely scheme 'P1' and 'P2' are tested. Table 4.6 shows the steps involved in these approaches, implemented by writing the task in APD (see Appendix C for sample task for scheme P1).

Table 4.6 Steps in startup schemes P1 and P2 for a distillation column.

Scheme P1	Scheme P2
Put all controllers on manual mode	Put all controllers on manual mode
Add feed to the column i.e. 16794 kg/h	Add feed to the column i.e. 16794 kg/h
Wait till the column sump fills up to 2.6 m and then turn off the column feed	Wait till the column sump fills up to 2.6 m and then turn off the column feed
Put the pressure controller in auto mode	Put the pressure controller in auto mode
Open the column vent valve to purge the nitrogen to expel the air sucked in, if any	Open the column vent valve to purge the nitrogen to expel the air sucked in, if any
Increase reboiler temperature gradually (e.g. 8 ^{o}C/min) and wait for 0.1 h after each step	Put the reboiler temperature controller on automatic mode and set it at 250^{o}C
Start the column reflux	Start the column reflux
Continue increasing steam temperature	Close vent valve when N_2 is purged
Close vent valve when N_2 is purged	Put the reflux drum level control into auto mode
Put the reflux drum level control on auto mode	Add more feed until the sump fills in
Add more feed until the sump fills in to 2.6 m	Wait until the reflux drum fills in and put the sump level controller on auto mode
Continue increasing steam temperature	Start the column feed
Wait until the reflux drum fills in and put the sump level controller to auto mode	Increase the reflux to the final value
Start the column feed	Change the reflux level and sump level set points to their final values (0.36 m and 1.64 m, respectively)
Increase the reflux to the final value	
Put the reboiler temperature controller to auto mode	
Change the reflux and sump level set points to their final values (0.36 m and 1.64 m, respectively)	

In scheme 1, a stepwise increase in the reboiler duty is employed and the temperature control ‘TC204’ is put on automatic mode only at the end. On the other hand, in scheme P2, TC 204 is put on automatic mode right at the beginning. Condenser temperature, condenser duty, mass fraction of biodiesel, reboiler temperature, reboiler duty, sump level, liquid flow from reboiler, vapor flow from reboiler, liquid flow from condenser are depicted in the Figures 4.9a-4.9i, respectively.

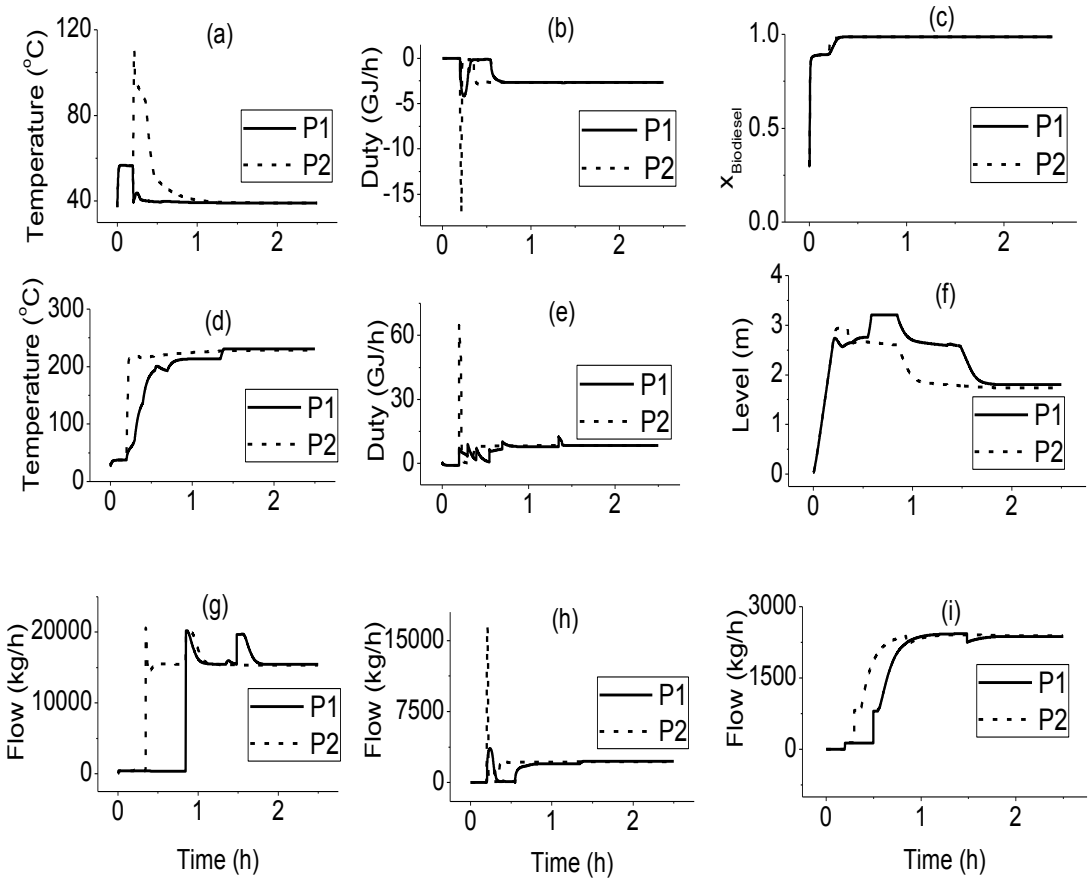

Figure 4.9 Transient profiles in the startup of FRAC3 by schemes P1 and P2: (a) condenser temperature, (b) condenser duty, (c) mass fraction of biodiesel, (d) reboiler temperature, (e) reboiler duty, (f) sump level, (g) liquid flow from reboiler, (h) vapor flow from reboiler, and (i) liquid flow from condenser.

As it can be noticed from the plots, P1 shows a smooth and gradual variation in these variables as opposed to that for P2, where spikes are observed in condenser temperature (Figure 4.9a), condenser duty (Figure 4.9b), reboiler duty (Figure 4.9e) and vapor flow from reboiler (Figure 4.9h). Behaviour of some of the variables in P2 may be unachievable and potentially dangerous in real practice due to the sudden increase in temperature and vapor flow in the column arising from putting TC 204 on automatic mode right at the beginning when error between process variable and set point is large. This also leads to large bumps in the process variables, as depicted in Figure 4.9. However, the settling time observed for P2 (for example, close to 1 h for sump level) is lesser that that found for P1 (close to 1.8 h for sump level). Note that the startup time also depends on the time a trainee waits after each step. It is clear from the figure that a stepwise increase is desirable. However, to optimize the step size, more scenarios can be tested. This is only feasible on an OTS as doing it in a real plant will be very expensive and hence unfavourable.

4.5.2 Interlock in Distillation Column FRAC-3

Interlock is a mechanism that is used to help prevent any harm to the operator or any damage to the system itleft by taking the action (e.g. stopping the equipement or utility flow) when tripped. Typically, a chemical plant has several interlocks (i.e. safety interlock or process interlock) in place. One such interlock has been simulated for FRAC3, where the utility trips when the reboiler temperature breaches 250^{o}C as biodiesel decomposes above 250^{o}C. The feed flow drops to 25% (from 16794 kg/h to 4198.5 kg/h) at 2 h. Reboiler temperature shoots up to 250^{o}C from 230^{o}C. Consequently, the utility trips and temperature falls. This is simulated by writing the

tasks in APD. The simulation displays '*UTILITYTRIP encountered due to reboiler temperature shoot up'* (see Appendix C). At 2.3 h, feed and utility are resumed manually.

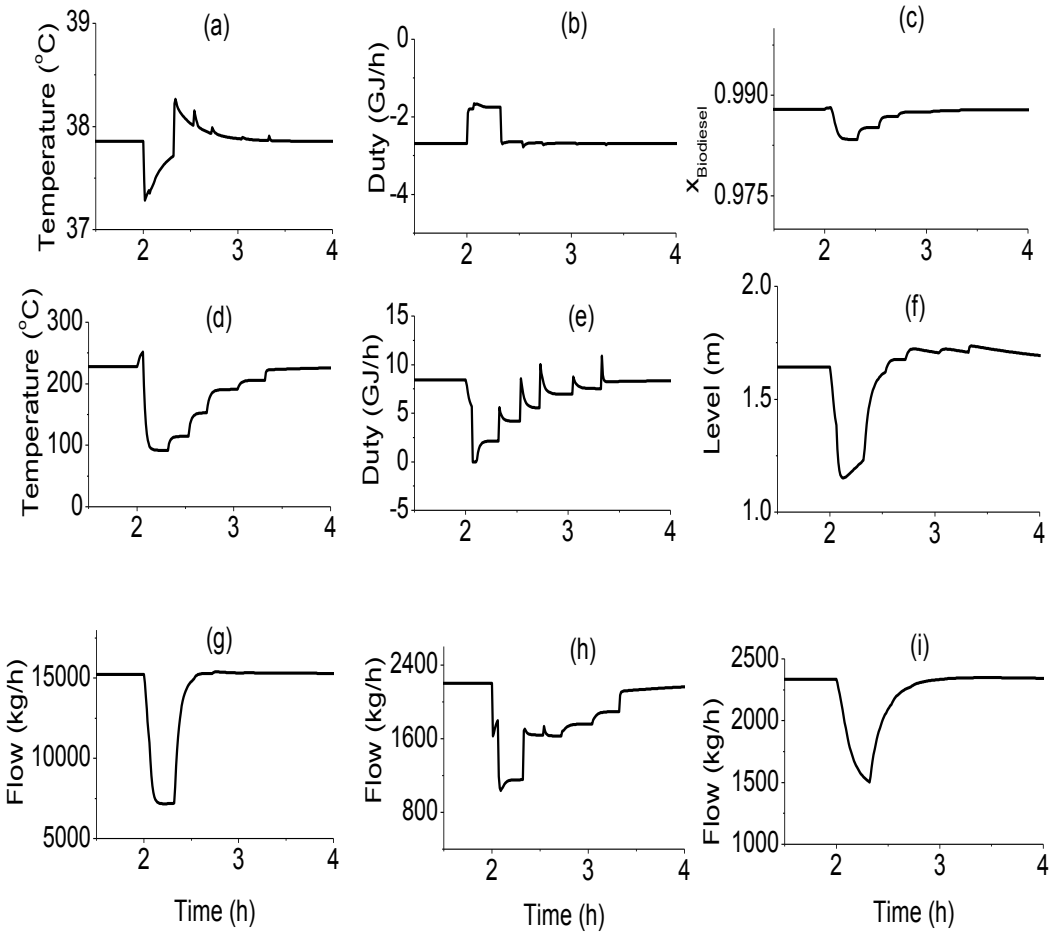

Figure 4.10 Transient profiles due to interlock trip on the reboiler temperature for the column: (a) condenser temperature, (b) condenser duty, (c) mass fraction of biodiesel, (d) reboiler temperature, (e) reboiler duty, (f) sump level, (g) liquid flow from reboiler, (h) vapor flow from reboiler, and (i) liquid flow from condenser.

The utility temperature is increased in stepwise manner to obtain bumpless transition. Transient profiles of condenser temperature, condenser duty, mass fraction

of biodiesel, reboiler temperature, reboiler duty, sump level, liquid flow from reboiler, vapor flow from reboiler and liquid flow from condenser are shown in Figures 4.10a-4.10i, respectively. Stabilization time and smoothness will depend on the manner in which a trainee ramp ups the utility. Using OTS, trainees can get aquainted with operation of the process by trying and testing different ramp up steps. Smaller steps would lead to smooth but slow response. On the other hand, the larger steps would lead to the bumps.

4.5.3 Reflux Failure in Distillation Column 'FRAC-3'

Reflux failure in FRAC3 (i.e. distillation column separating biodiesel from methanol in the transesterification section, see Figure 3.9) scenario is depicted in Figure 4.11. The instructor imparts a fault such that the reflux fails in FRAC3 at 2 h. Figure 4.11a shows that biodiesel flowrate reduces at 2 h as the liquid and vapour flow rates on trays (Figure 4.11e) and bottom flow rate (Figure 4.11c) decrease due to the reflux failure.

The variations in reflux drum, condenser and reboiler are presented in Figures 4.11b, 4.11d and 4.11f, respectively. Eventually, the trainee notices the effect and checks for the causes based on his understanding. Some of the possible causes include reflux pump failure, reflux valve failure, leakage, reflux drum dry-up and flow sensor's fault. Note that the ability of a trainee would depend on the extent of training he has undergone, and this will indeed decide how quickly he takes the right action.

In this case, the failure is due to the failure of reflux pump. At 2.3 h, the trainee switches on the standby pump to reconnect the reflux. The effects of reconnection of reflux are apparent from the transient profiles in Figure 4.11. The biodiesel product stabilizes at about 2.4 h.

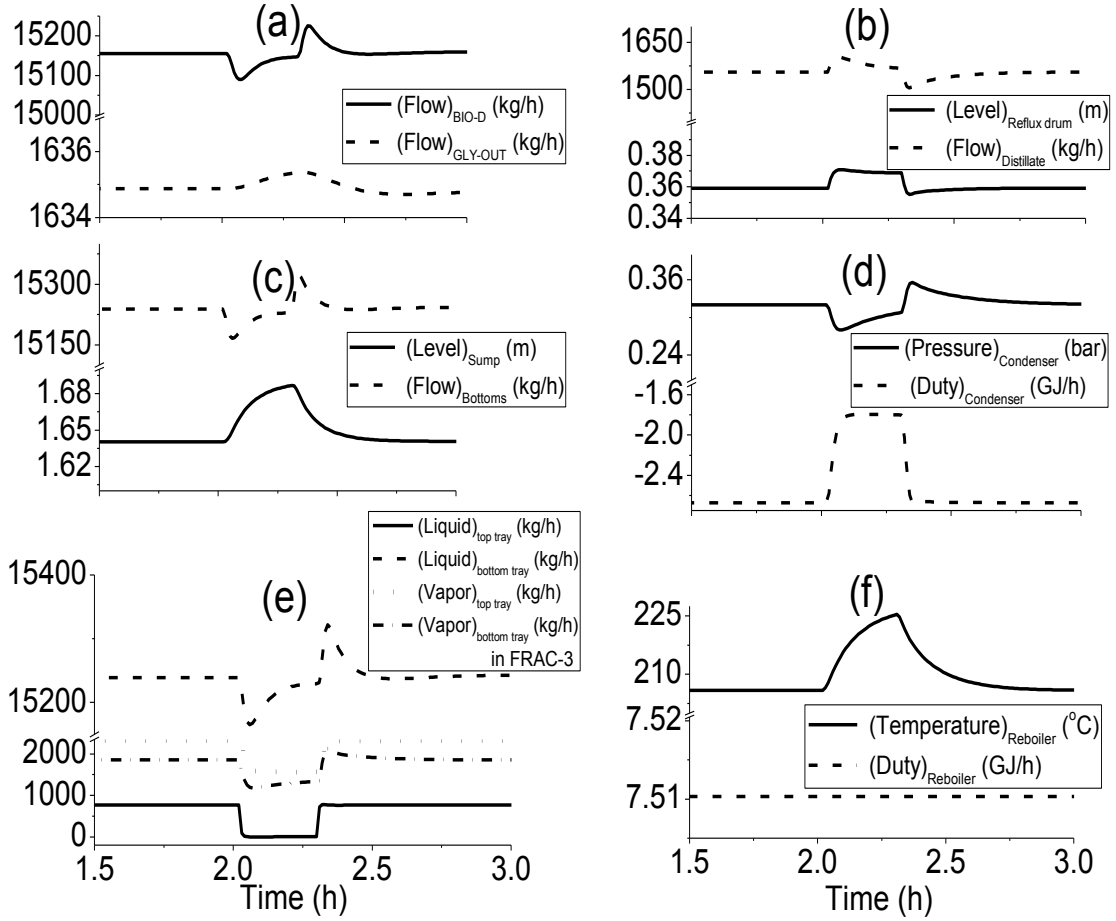

Figure 4.11 Transient profiles due to reflux failure in FRAC3 (correct action): reflux fails from 765 to 0 kg/h at 2 h, a trainee switches the standby pump on at 2.3 h and reflux resumes.

The wrong action by a trainee would make things worse; this is depicted for this example in Figure 4.12. In this case, a trainee notices the decrease in flows from trays in FRAC3. Without investing a root cause, the trainee increases the feed flow by 2% at 2.5 h to compensate the decrease in flows. Consequently, the process neither comes back to the original steady state nor stabilizes any sooner.

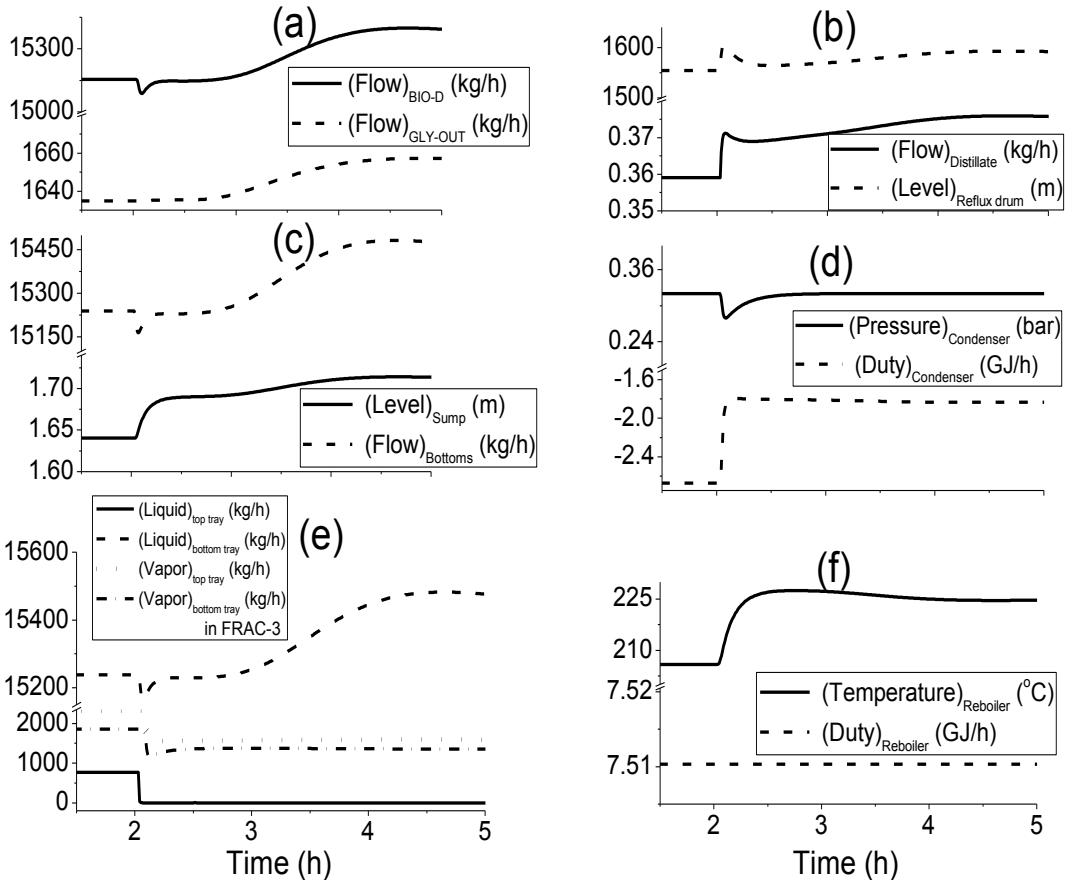

Figure 4.12 Transient profiles due to reflux failure in FRAC3 (incorrect action); reflux fails from 765 to 0 kg/h at 2 h, and a trainee increases the feed by 2% at 2.5 h without noticing the reflux pump failure.

4.5.4 Utility Failure in the CSTR 'RTRANS1'

As a part of OTS training, a scenario of utility failure in CSTR is simulated in APD. Figure 4.13 presents biodiesel flow, glycerol flow, biodiesel purity, mass fraction of biodiesel in stream 'R1', temperature in RTRANS1 and utility supply. The process is steady up to 2 h, at which utility supply fails.

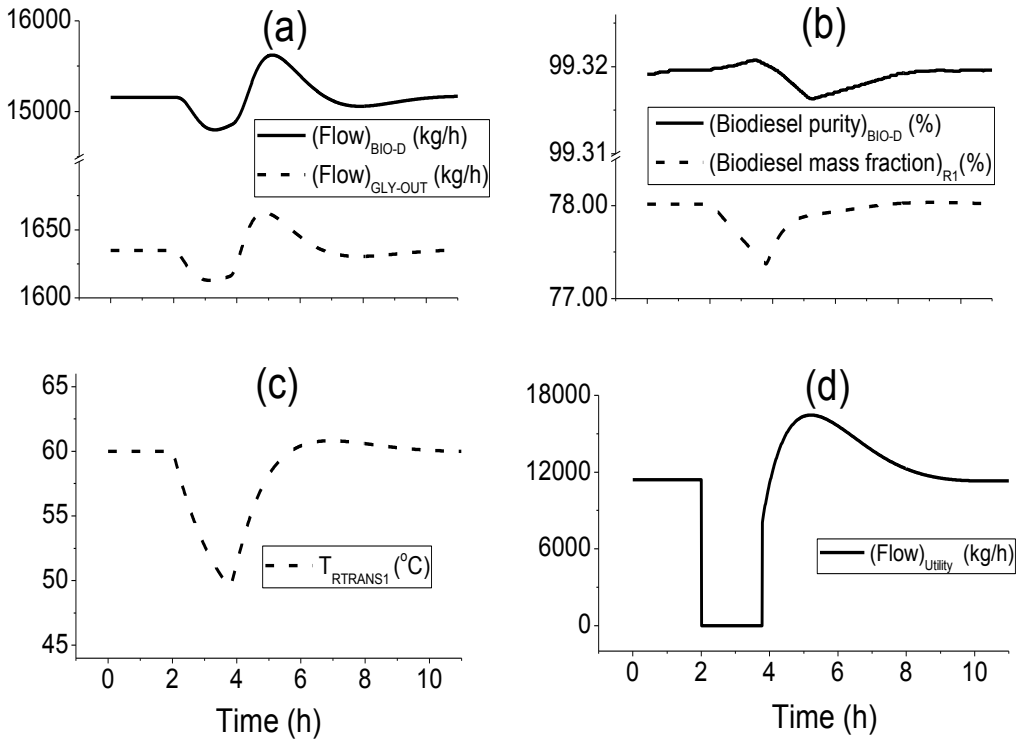

Figure 4.13 Utility failure in RTRANS1: utility fails at 2 h, temperature of RTRANS1 decreases to 50^{o}C and steam resumes at 4 h.

Consequently, temperature of the transesterification reactor 'RTRANS1' falls from 60^{o}C to 50^{o}C. This is to be noticed by a trainee and check for possible causes. The potential causes may be temperature sensor fault, sudden feed increase, utility failure etc. In present case, a trainee notices the fault and observes the root cause as

utility failure. At 4 h, the fault is corrected and the utility supply is resumed. Mistaken identification of the cause for reactor temperature fall, where a trainee reduces the feed to reduce the level in RTRANS1, was also simulated (not shown for brevity). This does not bring the process back to the original steady state and results in the loss of biodiesel product quantity and purity.

4.5.5 Pump 'P-1' Malfunction

A scenario of pump malfunction is simulated in APD. Figure 4.14 shows biodiesel flow, glycerol flow, biodiesel purity, mass fraction of biodiesel in RFFA, level in RFFA, flow from RFFA, level in phase separator 'W-1' and flow from W-1. The process is steadily operated up to 2 h, at which the fault in pump 'P-1' (in Figure 3.9) is imparted (i.e., P-1 is stopped). The purpose of this pump is to increase the pressure of the inlet stream to RFFA reactor. P-1 malfunction reduces the feed to RFFA from 16181 kg/h to 8175 kg/h. The P-1 malfunction can also be recognised by the reduction in the level of RFFA and W-1. This is to be observed by a trainee, who would look for potential factors causing it (for example, fault in flow/level sensor, reduction in WCO supply, sudden opening of the valve 'V-42', P-1 failure/malfunction etc).

In this case, a standby pump 'P-1-STANDBY' (Figure 4.15) is switched on at 2.25 h as the fault was imparted in the pump 'P-1'. Eventually, the process reaches its original steady state. Also, it can be seen that biodiesel flow rate does not change much; this is due to the fact that it is produced in a small amount in RFFA. Note that major portion of WCO i.e. triglycerides (about 94 %) converts to the biodiesel in the

transesterification section that follows the esterification section. Another action, where a trainee turns ‘LC100’ on manual mode and reduces the opening of valve ‘V-42’ to counter the reduction in the level of RFFA (not shown for brevity), is also performed. This is clearly a wrong judgement on the part of a trainee as the reduction in the level of RFFA was due to the malfunction in the ‘P-1’. In this case, instead of returning to the original steady state, the process settles to the another steady state with lower biodiesel production. However, no major change is observed in the biodiesel purity; this is due to the high conversion of FFAs in RFFA despite reduction in the level.

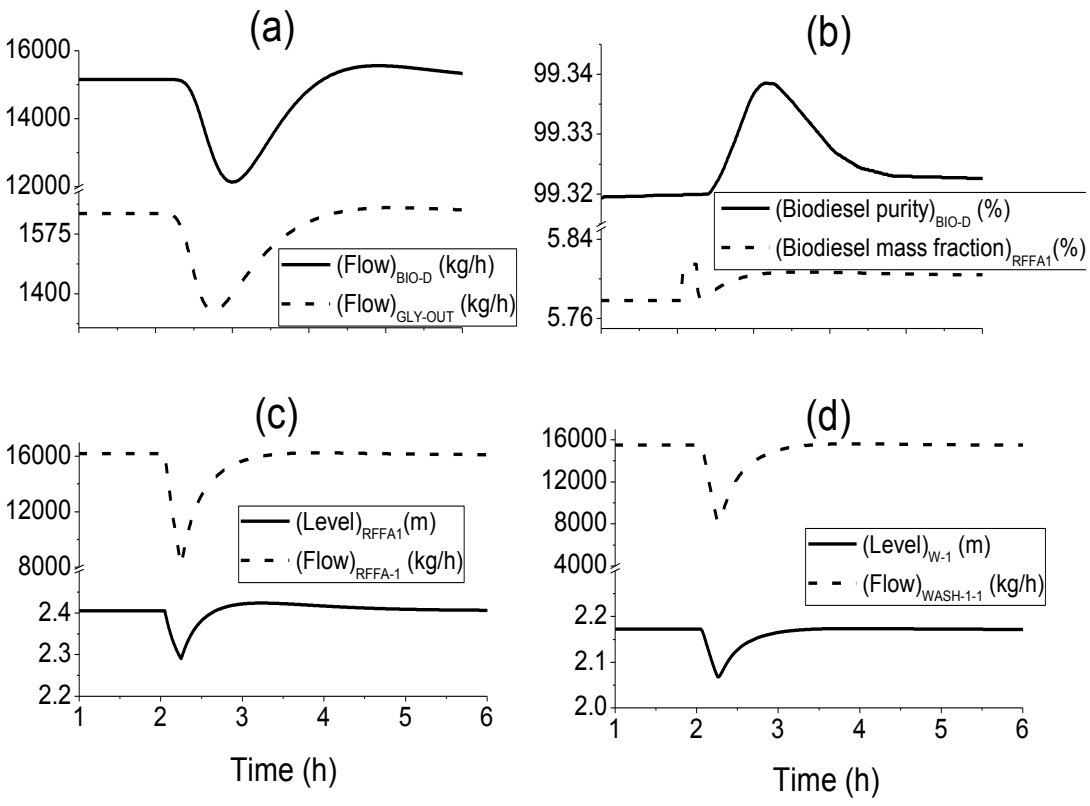

Figure 4.4 Pump failure: malfunction in P-1 at 2 h reduces the flow from 16181 kg/h to 8175 kg/h, and standby pump started at 2.25 h

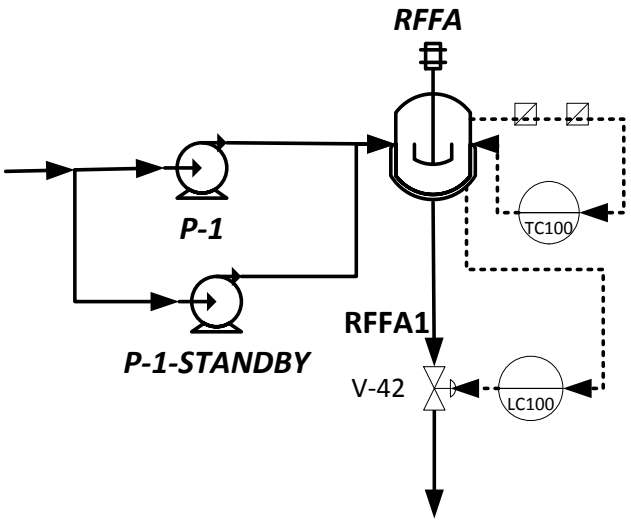

Figure 4.15 Schematic showing the standby pump.

4.5.6 Valve ‘V-16’ Malfunction

A malfunction in valve is imparted for OTS training on the biodiesel plant in APD. Figure 4.16 presents biodiesel flow, glycerol flow, biodiesel purity, mass fraction of biodiesel in R1, level in RTRANS1, flow from RTRANS1, level in phase separator ‘D-1’ and flow from D-1. At 2 h, malfunction is simulated for the valve ‘V-16’ (in Figure 3.9). V-16 goes wide open and increases the flow of stream ‘R1’ from 18750 kg/h to 37500 kg/h.

This can be noticed by the decrease of level in RTRANS1 and the increase in the level of D-1. Observing this, a trainee searches for possible reasons (e.g., fault in flow/level sensors, variation in WCO supply, controller malfunction, sudden opening of the valve ‘V-16’ etc). In this example, a bypass valve in the bypass line (Figure 4.17) is used at 2.4 h as the valve ‘V-16’ had gone wide open and stuck there.

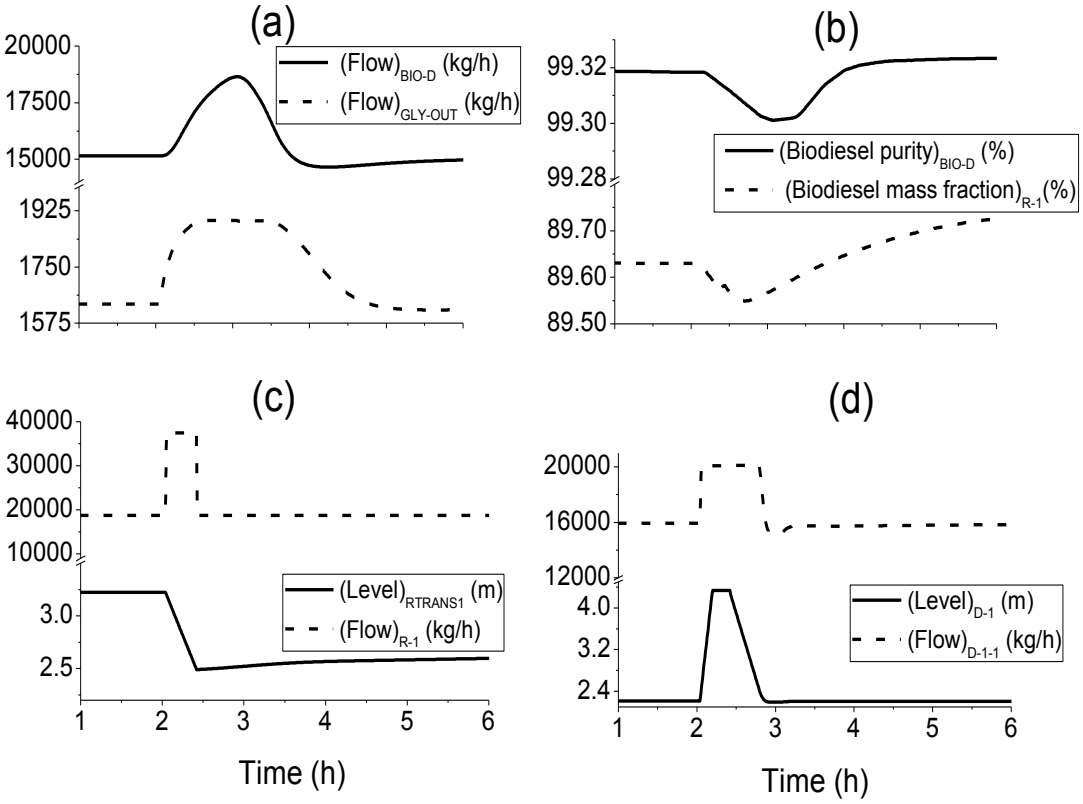

Figure 4.16 Valve failure: valve 'V-16' goes wide open to 100% (flow increases from 18750 to 37500 kg/h in outlet of RTRANS1 at 2 h, and bypass line is used at 2.4 h).

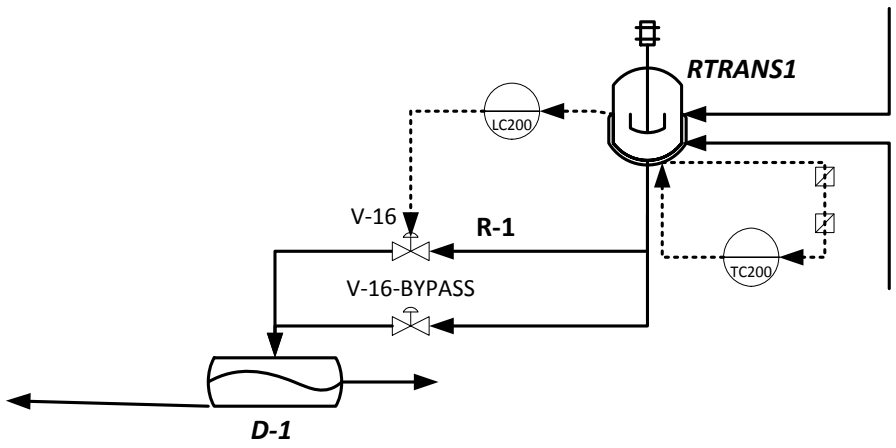

Figure 4.17 Schematic showing the bypass valve.

Eventually, the process stabilizes and reaches to its original steady state. As it was done in other scenarios, a wrong action by a trainee was also tested where a trainee reduces the set pint of 'LC104' to counter the reduction in the level of RTRANS1 (not shown for brevity). This results in the unstable process operation and biodiesel product loss. Therefore, timely intervension and correct action is inevitable for the smooth and safe process operation.

4.5.7 Effect of fire in Flash Vessel 'F-1'

Equipment catching fire can cause havoc in a process plant. Proper safety procedures should be in place to minimize the damage. The venting required (Eq. 4.5) due to over pressurization can be determined by API 2000 guidelines (Eqs. 4.1-4.4), which is applicable for sub-atmospheric vessels. Note that pressure relief devices can protect the unit operation against overpressure only; they do not protect it against structural failure when it is exposed to exceedingly high temperatures as in case of Fire. Figure 4.18 depicts the effect of fire in flash vessel 'F-1'.

Total heat of absorption (input) to the wetted surface (Q) using Eq. 4.1, temperature (T), pressure (P), wetted wall surface area used for heat load calculation (A_w), liquid level used in fire calculation, liquid holdup and flow through PSV are presented in Figure 4.18. Process runs steadily up to 2 h. T, P and Q increase after 2 h as a result of F-1 catching fire. Q is calculated based on API 2000 guidelines as given below (API, 1987). Also, A_w, level and holdup decrease gradually due to the liquid vaporization. Flow through PSV is the result of PSV actions arising due to the

increase in pressure. PSV is set to open at 1.5 bar. At about 5 h, pressure comes back to 1.5 bar and Q remains constant. The equation used for the heat load varies depending on the size of wetted area.

$$Q = 20000FA_w \quad \text{for up to 200 ft}^2 \tag{4.1}$$

$$Q = 63150FA_w \quad \text{for up to 18.6 m}^2 \tag{4.2}$$

$$Q = 199300FA_w{}^{0.566} \quad \text{for } 200\text{ft}^2 < A_w \leq 1000\ \text{ft}^2 \tag{4.3}$$

$$Q = 963400FA_w{}^{0.338} \quad \text{for } 1000\text{ft}^2 < A_w \leq 2800\ \text{ft}^2 \tag{4.4}$$

In the above equations, Q is the total heat of absorption (input) to the wetted surface, in Btu/hr, F is the environmental factor (whose value for various types of insulation and drainage are given in API-2000, and A_w is the total wetted surface area in square feet calculated as follows (API, 1987).

- Horizontal vessels: 75% of area of vessel at height equal to or less than 30 ft above the source of flame.
- Vertical vessels: Vessel area up to 30 ft above the source of flame. (Surface area of vessel's bottom is not included if the vessel is not above the source of flame i.e. grade).

For wetted area larger than 2800 ft², it was concluded that no further venting would be required as complete fire involvement is unlikely. However, for all refrigerated tanks, regardless of design pressure, and for non-refrigerated tanks designed for pressure over 1 psig, additional venting is desirable because liquids will be close to their boiling points and Eq. 4.1 is used. The venting required can be found using the following equation:

$$Venting\ (SCFH) = 3.091 \times \frac{QF}{L} \times \left(\frac{T}{M}\right)^{0.5} \quad (4.5)$$

where SCFH is the venting requirement in standard cubic feet per hour, Q is the heat input from fire exposure in BTU per hour, L is the latent heat of vaporization of the stored liquid at the relieving pressure and temperature in BTU per pound, T is the temperature of the relieving vapor, in degrees Rankine (this is normally assumed to correspond to the boiling point of the stored fluid at the relieving pressure) and M is the molecular weight of the vapor being relieved.

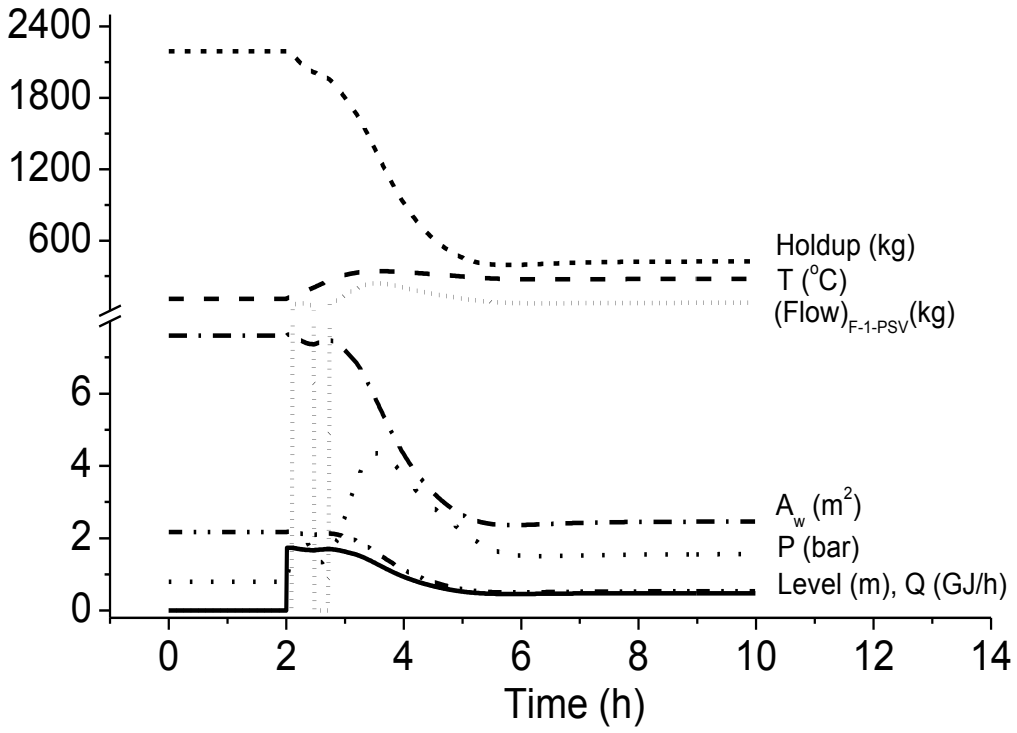

Figure 4.18 Effect of fire in flash vessel 'F-1' (API 2000).

4.5.8 Pressure Safety Valve in 'F-1'

Pressure safety valves (PSV) play a crucial role in maintaining safety in process plants. A variety of factors may lead to the over pressurization of the unit operations. PSV is implemented with a very small leak when the device is closed because a non-zero value is required for convergence in APD. The flow rate of this leak is insignificant compared to the relief rate. PSV can support reverse flow, calculate subcritical and critical flow and model single- or two-phase flow. Ideal nozzle (homogeneous equilibrium model) proposed by Design Institute for Emergency Relief Systems (DIERS) is used for flow calculations (Fisher et al., 1992). PSV is assumed to be 'conventional-type', i.e., a spring loaded valve whose operational characteristics are directly affected by changes in the back pressure as opposed to a 'balanced-type' valve, which is a spring loaded valve that incorporates a bellows or other means for minimizing the effect of back pressure on the operational characteristics of the valve. Hysteresis of 'F-1-PSV' is presented in Figure 4.19. Design details of F-1-PSV are given in Table 4.7.

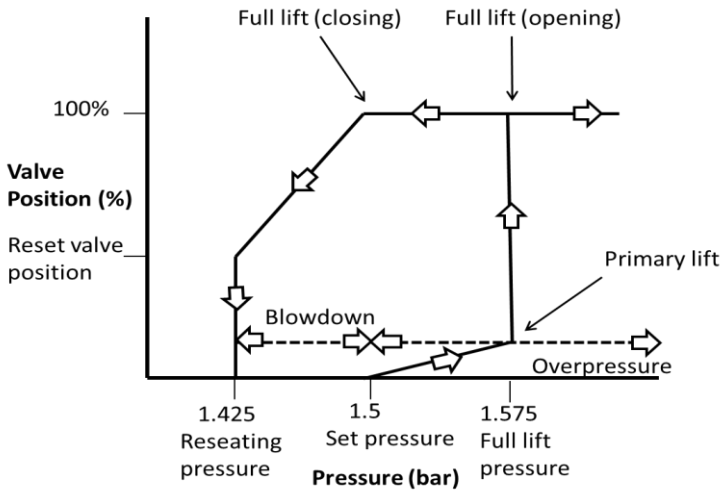

Figure 4.19 Hysteresis in the PSV 'F-1-PSV' (Aspen Technology, 2014).

Figure 4.20 presents the PSV in ‘F-1’ (in Figure 3.9) that is simulated in APD. Process runs steadily up to 2 h, when pressure controller ‘PC-103’ is set to manual mode and valve ‘V-12’ is closed that leads to the over pressurization in F-1. PSV is set to open at 1.5 bar, after which pressure begins to come down. Later, a trainee needs to intervene to bring back the process to original steady state. Trainee manually opens V-12 to 50%.

Then at 4.3 h, PC-103 is turned to auto mode. Process reaches back to the original state in about 5 h. Note that pressure has faster dynamics and hence step size for time may have to be significantly reduced to capture dynamics. Also, it is found to be essential in APD to run it without fail.

Table 4.7 Design details of F-1-PSV.

Valid phases	**Vapor-liquid**
Valve characteristics	Linear
Flash calculation	Constant enthalpy
Flow calculations method	Ideal HEM (DIERS)
Valve type	Conventional
Throat Diameter (m)	0.01
Inlet Diameter (m)	0.012
Outlet Diameter (m)	0.013
Set pressure (bar)	1.5
Full lift pressure (opening)	1.575
Reseating pressure	1.425

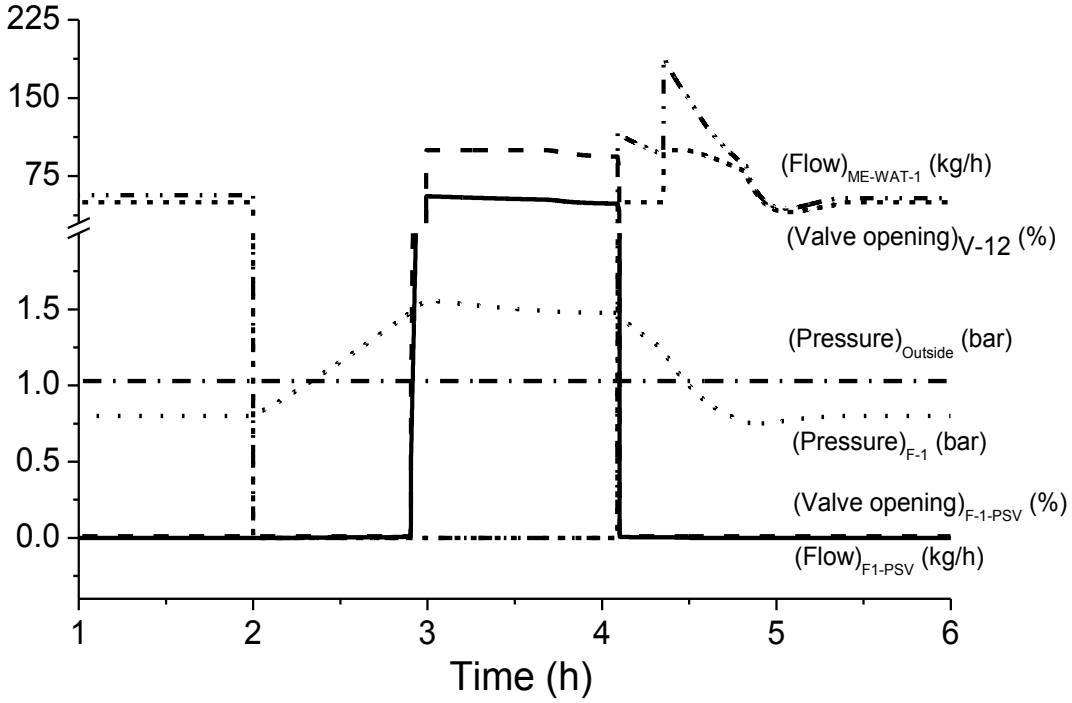

Figure 4.20 Pressure safety valve in the flash vessel: at 2 h, 'V-12' is closed to 0; PSV becomes active eventually when P=1.5 bar; at 4.1h, overhead valve is manually opened to 50%, and pressure controller 'PC-103' is put on auto mode at 4.3 h.

4.5.9 Bursting Disk in Flash Vessel 'F-1'

To cope with over pressurization in the unit operation, bursting disk can be used in place of PSV. Figure 4.21 depicts the scenario where bursting disk is used in 'F-1'. The main difference between PSV and bursting disk is that PSV maintains the pressure at the set point in contrast to bursting disk where the system pressure reaches the atmospheric pressure after the burst. Pipe diameter is 0.12 m and orifice diameter is 0.05 m. Similar to the study carried out in the previous section, 'V-12' is

closed at 2 h that leads to over pressurization. Bursting disk bursts at 1.5 bar, and brings the system pressure to atmospheric pressure.

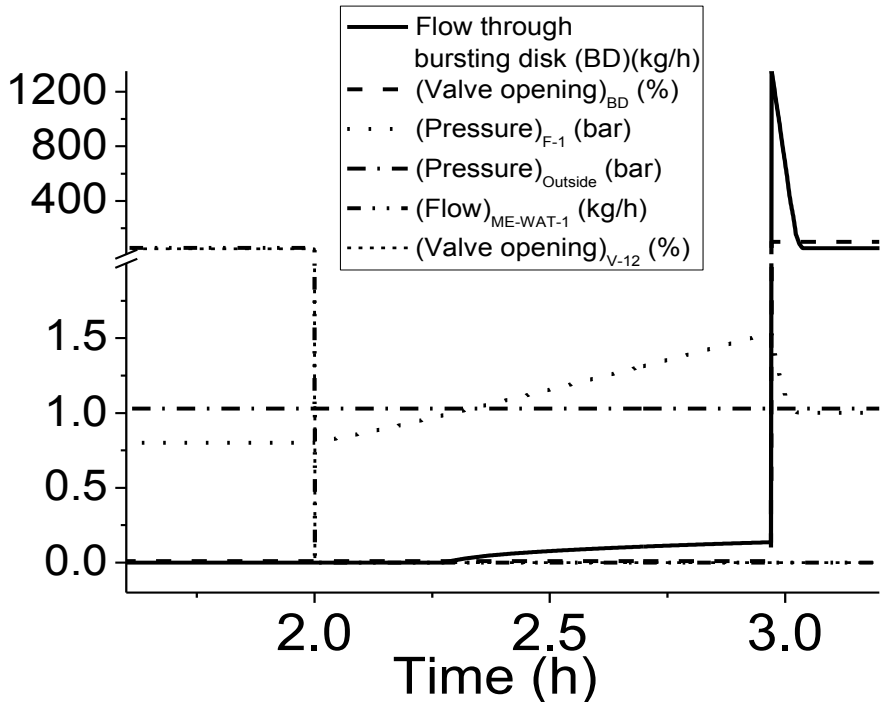

Figure 4.21 Bursting disk in the flash vessel: at 2 h, overhead valve closed to 0, bursting disk becomes active when P = 1.5 bar, burst occurs at 3h and system pressure reaches 1 atm.

4.5.10 Effect of fire in CSTR 'RFFA'

Fire can be disastrous in any process plant. Proper safety measures should be available to contain the fire. Also, they should be put in place to cope with the over pressurization in unit operations. Figure 4.22 depicts the effect of fire in CSTR 'RFFA'. Total heat of absorption (input) to the wetted surface (Q) using Eq. 4.7., temperature (T), pressure (P), wetted wall surface area used for heat load calculation (A) and liquid level used in fire calculation are presented in Figure 4.22 up to 10 h.

Process is run steadily up to 2 h, when T, P and Q increase as a result of RFFA catching the fire. Q is calculated based on API 521 guidelines (Eqs. 4.6, 4.7) as given below (API, 1990; Aspen technology, 2014); this is applicable for maximum allowable working pressure greater than 15 psig.

Heat absorption (Q) across the wetted surface of a vessel is given by:

$$Q = 21000FA_w{}^{0.82} \tag{4.6}$$

when there are prompt fire-fighting efforts and drainage, and

$$Q = 34500FA_w{}^{0.82} \tag{4.7}$$

when adequate fire-fighting efforts and drainage do not exist. In these equations, Q is the total heat of absorption (input) to the wetted surface, in Btu/hr, F is the environmental factor, and A_w is the total wetted surface in square feet at height equal to or less than 25 ft above the source of flame. Note that A_w is the area wetted by the vessel liquid contents, which is effective in generating vapor when the area is exposed to fire. Only that portion of the vessel that is wetted by the internal liquid and is equal to or less than 25 ft above the source of flame needs to be employed. The variations of pressure in Figure 9 is due to the response of 'RFFA-PSV' (see Figure 3) having the set point of 5 bar, at which the PSV becomes active. PSV is employed to cope with over pressurization in CSTR 'RFFA'. Design details of 'RFFA-PSV' are given in Table 1. Hysteresis of 'RFFA-PSV' is presented in Figure 10. PSV opens at the set pressure i.e. 5 bar, after which pressure in RFFA begins to come down. Flow through RFFA-PSV is the result of PSV opening that is based on hysteresis presented in Table 1 and Figure 10. PSV opens fully when the pressure

reaches 5.25 bar and closes fully when the pressure reaches 4.75 bar. Note that outside pressure is constant at 1.013 bar.

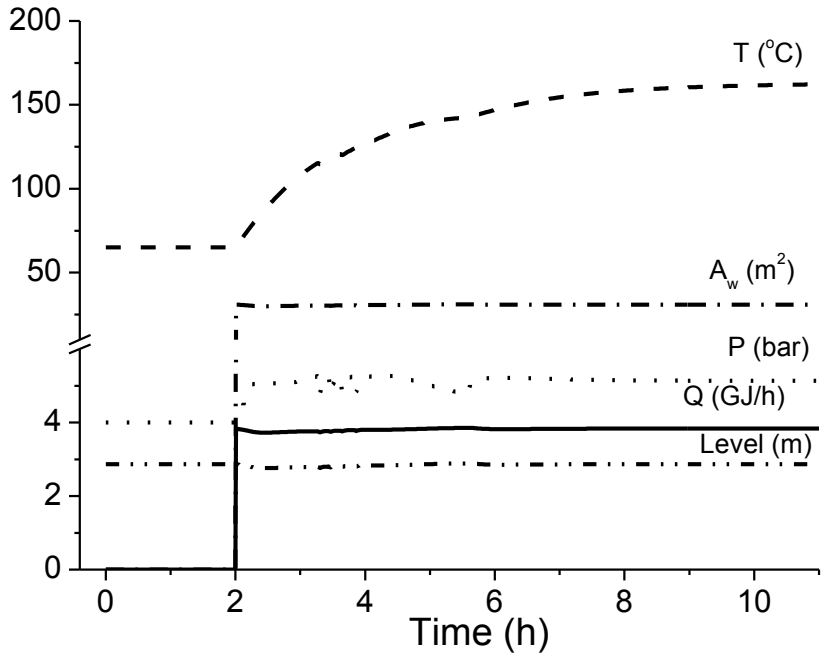

Figure 4.22 Effect of fire in the CSTR 'RFFA' (following API 521 guidelines).

4.5.11 PSV in CSTR 'RFFA'

PSV is employed to cope with over pressurization in CSTR 'RFFA'. Design details of 'RFFA-PSV' are given in Table 4.8. Hysteresis of PSV 'RFFA-PSV' is presented in Figure 4.23. Figure 4.24 presents the application PSV in the esterification reactor 'RFFA'. At 2h, fire leads to the over pressurization in RFFA. Consequently, PSV opens at the set pressure i.e. 5 bar, after which pressure begins to come down. Flow through RFFA-PSV is the result of PSV opening that is based on hysteresis presented in Table 4.8 and Figure 4.23. Note that outside pressure is constant at 1.013 bar.

Table 4.8 Design details of ‘RFFA-PSV’.

Valid phases	**Vapor-liquid**
Valve characteristics	Linear
Flash calculation	Constant enthalpy
Flow calculations method	Ideal HEM (DIERS)
Valve type	Conventional
Throat Diameter (m)	0.06
Inlet Diameter (m)	0.07
Outlet Diameter (m)	0.08
Set pressure (bar)	5
Full lift pressure (opening)	5.25
Reseating pressure	4.75

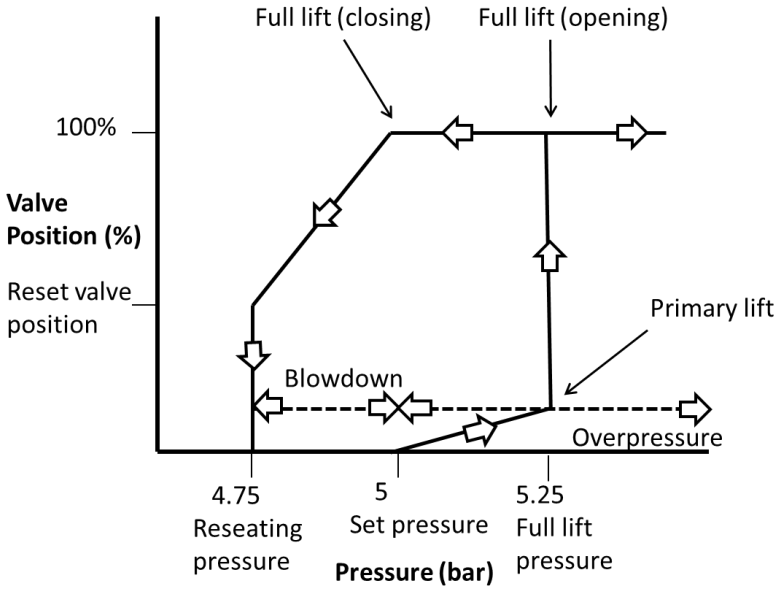

Figure 4.23 Hysteresis in the PSV ‘RFFA-PSV’.

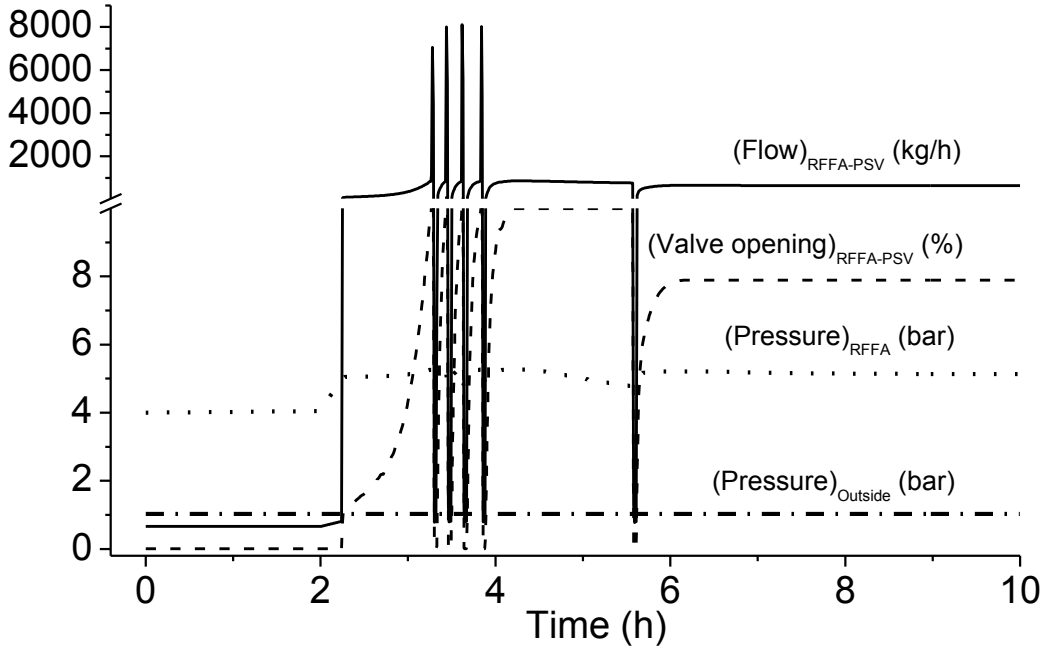

Figure 4.24 PSV in the CSTR 'RFFA': at 2 h, pressure increases due to fire, and PSV becomes active when P=5 bar.

4.6 Summary

In summary, this chapter presents and explains the outcome of the methodology followed in chapter 3. Firstly, two alternative processes are developed and compared against respective literature. Then, the camparison is carried out for the extended capacity. Trade-offs between multiple objectives, such as profit, heat duty and organic waste resulted from the constrained MOO of biodiesel process are then discussed. Pareto-optimal fronts between objectives and trends of decision variables with respect to profit are presented. Based on this, a comparison is carried out between two processes meticulously and better process alternative is determined.

Later, the results of PWC for the chosen process are discussed and performance is evaluated based on settling time, DPT and TV. For several disturbances, the PWC system is able to maintain biodiesel purity under control as per EN standards, and is found to provide smooth, stable and robust control. Transient profiles for several process variables are also presented for differernt disturbances. In the end, results of OTS for several scenarios are discussed. The scenarios studied are: equipment malfunctions, fire, pressure safety valve, bursting disk, interlock and startup. The developed OTS is found to be able to replicate the process behaviour for these scenarios. To show the capability of developed OTS in APD, one correct and one wrong action that would be taken by trainees, are simulated. Effect of such actions on process operation and biodiesel product are then discussed. In essence, these scenarios present the in-depth understanding of the process under startup and emergency events. In addition, HAZOP analysis is carried out as presented in the Appendix D. Next chapter lists the conclusions arrived from this study and recommendations for future work in this field.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This section presents the findings of this research. This study concludes with the following conclusions:

This study develops an OTS for the homogeneously catalyzed two-step biodiesel process. Firstly, two alternative alkali-catalyzed biodiesel production processes are simulated in Aspen Plus considering detailed reaction kinetics and detailed constituents of oil. Both processes use waste cooking palm oil as the feed, which is favourable from the point of both economic feasibility and environmental impact. Steady state simulation results have been validated against literature dat and found to be reasonable. Two bi-objective problems are solved using EMOO program incorporating NSGA-II, to investigate the performance of both the process alternatives. Trade-offs between profit and heat duty, and profit and organic waste are analyzed, which examine profitability and environmental impact of biodiesel processes. Improvement in the profit is accompanied by increase in heat duty, and also with increased formation of organic waste. The main contributor to these increases is WCO flow rate.

Process 1 having three transesterification reactors produces significantly lower organic waste (by 32%), requires lower heat duty (by 39%) and slightly more profitable (by 1.6%) compared to Process 2 having a single transesterification reactor

and also a different separation sequence. Overall, the obtained quantitative trade-offs between objectives enable better decision making about the process design for biodiesel production from waste cooking oil. Also, the effect of using detailed components of oil versus lumped components is analyzed and found to have some impact. Hence, considering detailed composition of oil with detailed reaction kinetics is recommended for biodiesel process simulation, for obtaining more realistic results. Better process in terms of higher profit and lower environmental impact is determined. Main features of the selected process are: (1) one reactor for esterification, (2) three reactors for transesterification with intermediate phase separators, and (3) biodiesel and glycerol are separated first followed by methanol separation and washing of biodiesel. This scheme prevents backward reactions as methanol is present until biodiesel and glycerol are separated, and the recovered methanol contains a very small amount of water, which avoids energy intensive methanol-water separation and facilitates methanol re-use in the process. Also, the chosen process is close to that used in the industry.

Later, a suitable PWC structure using IFSH methodology, and an OTS using APD are developed for the concerned process. Next, a dynamic simulator is developed for the chosen process. Dynamics of the process has been studied for several disturbances. This is important for the development of the PWC structure development. Subsequently, a suitable PWC system is developed and evaluated for the chosen complex multiunit biodiesel process using WCO as the feedstock. The IFSH methodology is used to design a PWC system for the biodiesel process; in this, control loops are decided based on heuristics, simulations and ERGA analysis as this is a critical factor in the successful implementation of PWC. The main merits of

IFSH methodology are effective use of rigorous process simulators and heuristics in developing a PWC system, and simplicity of application. The performance of the designed control system is investigated in terms of settling time of biodiesel production rate, deviation from the production target (that affects economics) and total variation in manipulated variables (that depicts the control effort needed to stabilize the process), for a number of disturbances. For these disturbances, the PWC system is able to maintain biodiesel purity under control as per EN standards, and is found to provide smooth, stable and robust control.

Finally, an OTS is developed for biodiesel production from WCO. Aspen OTS Framework is used on top of APD simulation of biodiesel process. Several emergency situations were developed which can be inserted by the instructor at any point in time to train the operators. Several scenarios such as equipment malfunctions, fire, pressure safety valves, burst disk, interlock and startup are studied using the developed OTS. These process scenarios can be loaded and utilized at any point in time to train the new and existing operators. This is the first study to investigate the application of the commonly used Aspen Plus Dynamics in the OTS development for biodiesel production from WCO. Experience from this is useful for development of OTS for other processes and consequently increased operator training for safer plants.

In summary, the novelty of the present study are: 1) development and detailed simulation of a two-step homogeneously catalyzed biodiesel production from WCO, 2) MOO using NSGA-II, which is implemented in Excel and interlinked with Aspen Plus, 3) development and evaluation of a PWC system for the complex

homogeneously catalyzed two-step biodiesel production from WCO, and 4) OTS development for the concerned process using APD and Aspen OTS Framework. This is the first study to develop a complete PWC structure and OTS for a homogeneously catalyzed two-step biodiesel production from WCO.

5.2 Recommendations for Further Work

There are several recommendations for future research related to this thesis topic, and they are as follows.

(i) Thus far, biodiesel production using homogeneous catalyst is widely used. However, this process has some intrinsic drawbacks, namely, 3 phase (V-L-L) system formation, need of neutralization of acid and alkali catalyst, thus more number of process equipment, use of excess of methanol and hence its separation etc. Therefore, efforts should be directed to develop suitable processes which overcome these drawbacks.

(ii) MOO continues to be the major thrust area in chemical engineering. Stricter environmental regulations and economic competition drive companies to look for efficient design and operation of process. Although NSGA-II used in this study worked successfully to determine the optimal solutions for conflicting objectives, other evolutionary algorithms such as differential algorithm can be explored.

(iii) Numerous PWC methodologies and applications have been developed in recent years. As process industry is constantly evolving and facing new challenges everyday, PWC remains an active research area. Some promising areas of study in

the PWC domain are: Improvement of heuristics-based PWC methodologies and Integrated design and control.

(iv) In continuation of this study, a networked based training should be explored. Possibility of interlinking this simulator with real DCS/PLC should also be explored.

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APPENDIX A

Reaction Set A.1: Esterification reactions and their kinetics

1. $FFA-O + METHANOL \rightarrow METHYL-O + WATER$
2. $METHYL-O + WATER \rightarrow FFA-O + METHANOL$
3. $FFA-LIO + METHANOL \rightarrow METHY-LI + WATER$
4. $METHYL-LI + WATER \rightarrow FFA-LIO + METHANOL$
5. $FFA-P + METHANOL \rightarrow METHYL-P + WATER$
6. $METHYL-P + WATER \rightarrow FFA-P + METHANOL$
7. $FFA-M + METHANOL \rightarrow METHYL-M + WATER$
8. $METHYL-M + WATER \rightarrow FFA-M + METHANOL$
9. $FFA-S + METHANOL \rightarrow METHYL-S + WATER$
10. $METHYL-S + WATER \rightarrow FFA-S + METHANOL$

The value of pre-exponential factor and activation energy for reactions 1, 3, 5, 7, 9 is 3.913×10^5 $(kgmol\,K^{-n}/sec\,cum)/(kgmol/cum)^{\Sigma\alpha i}$) and 44558.8 J/mol, respectively; and for reactions 2, 4, 6, 8, 10 is 707.166 $(kgmol\,K^{-n}/sec\,cum)/(kgmol/cum)^{\Sigma\alpha i}$) and 42761.4 J/mol respectively.

Reaction Set A.2: Transesterification reactions and their kinetics (Aspen Technology, 2012)

1. $OOO + METHANOL \rightarrow METHYL-O + OO$
2. $OO + METHYL-O \rightarrow OOO + METHANOL$
3. $OO + METHANOL \rightarrow METHYL-O + 1-O$
4. $METHYL-O + 1-O \rightarrow OO + METHANOL$

5. $1-O + METHANOL \rightarrow GLYCEROL + METHYL-O$

6. $GLYCEROL + METHYL-O \rightarrow METHANOL + 1-O$

7. $MMM + METHANOL \rightarrow METHYL-M + MM$

8. $METHYL-M + MM \rightarrow MMM + METHANOL$

9. $MM + METHANOL \rightarrow METHYL-M + 1-M$

10. $METHYL-M + 1-M \rightarrow MM + METHANOL$

11. $1-M + METHANOL \rightarrow GLYCEROL + METHYL-M$

12. $GLYCEROL + METHYL-M \rightarrow METHANOL + 1-M$

13. $PPP + METHANOL \rightarrow METHYL-P + PP$

14. $METHYL-P + PP \rightarrow PPP + METHANOL$

15. $PP + METHANOL \rightarrow METHYL-P + 1-P$

16. $METHYL-P + 1-P \rightarrow METHANOL + PP$

17. $1-P + METHANOL \rightarrow GLYCEROL + METHYL-P$

18. $GLYCEROL + METHYL-P \rightarrow METHANOL + 1-P$

19. $PPS + METHANOL \rightarrow METHYL-S + PP$

20. $METHYL-S + PP \rightarrow PPS + METHANOL$

21. $PPS + METHANOL \rightarrow METHYL-P + PS$

22. $METHYL-P + PS \rightarrow PPS + METHANOL$

23. $PS + METHANOL \rightarrow METHYL-P + 1-S$

24. $METHYL-P + 1-S \rightarrow METHANOL + PS$

25. $1-S + METHANOL \rightarrow GLYCEROL + METHYL-S$

26. $GLYCEROL + METHYL-S \rightarrow METHANOL + 1-S$

27. $PS + METHANOL \rightarrow METHYL-S + 1-P$

28. $METHYL-S + 1-P \rightarrow METHANOL + PS$

29. $PPO + METHANOL \rightarrow METHYL-O + PP$

30. $METHYL-O + PP \rightarrow PPO + METHANOL$

31. $PPO + METHANOL \rightarrow METHYL-P + PO$

32. $METHYL-P + PO \rightarrow PPO + METHANOL$

33. $PO + METHANOL \rightarrow METHYL-P + 1-O$

34. $METHYL-P + 1-O \rightarrow METHANOL + PO$

35. $PO + METHANOL \rightarrow METHYL-O + 1-P$

36. $METHYL-O + 1-P \rightarrow PO + METHANOL$

37. $MMP + METHANOL \rightarrow METHYL-P + MM$

38. $MM + METHYL-P \rightarrow METHANOL + MMP$

39. $MMP + METHANOL \rightarrow METHYL-M + MP$

40. $MP + METHYL-M \rightarrow METHANOL + MMP$

41. $MP + METHANOL \rightarrow METHYL-P + 1-M$

42. $METHYL-P + 1-M \rightarrow MP + METHANOL$

43. $MP + METHANOL \rightarrow METHYL-M + 1-P$

44. $METHYL-M + 1-P \rightarrow MP + METHANOL$

45. $PPLI + METHANOL \rightarrow METHY-LI + PP$

46. $METHY-LI + PP \rightarrow PPLI + METHANOL$

47. $PPLI + METHANOL \rightarrow METHYL-P + PLI$

48. $METHYL-P + PLI \rightarrow PPLI + METHANOL$

49. $PLI + METHANOL \rightarrow METHY-LI + 1-P$

50. $METHY-LI + 1-P \rightarrow PLI + METHANOL$

51. $PLI + METHANOL \rightarrow METHYL-P + 1-LI$

52. $METHYL-P + 1-LI \rightarrow PLI + METHANOL$

53. $1-LI + METHANOL \rightarrow GLYCEROL + METHY-LI$

54. $GLYCEROL + METHY-LI \rightarrow METHANOL + 1-LI$

55. $POO + METHANOL \rightarrow METHYL - O + PO$

56. $METHYL - O + PO \rightarrow POO + METHANOL$

57. $POO + METHANOL \rightarrow METHYL - P + OO$

58. $METHYL - P + OO \rightarrow POO + METHANOL$

59. $POS + METHANOL \rightarrow METHYL - S + PO$

60. $METHYL - S + PO \rightarrow METHANOL + POS$

61. $POS + METHANOL \rightarrow METHYL - P + OS$

62. $METHYL - P + OS \rightarrow METHANOL + POS$

63. $POS + METHANOL \rightarrow METHYL - O + PS$

64. $METHYL - O + PS \rightarrow METHANOL + POS$

65. $PLIO + METHANOL \rightarrow METHYL - O + PLI$

66. $METHYL - O + PLI \rightarrow METHANOL + PLIO$

67. $PLIO + METHANOL \rightarrow METHYL - P + LIO$

68. $METHYL - P + LIO \rightarrow METHANOL + PLIO$

69. $PLIO + METHANOL \rightarrow METHY - LI + PO$

70. $METHY - LI + PO \rightarrow METHANOL + PLIO$

71. $LIO + METHANOL \rightarrow METHYL - O + 1 - LI$

72. $METHYL - O + 1 - LI \rightarrow LIO + METHANOL$

73. $LIO + METHANOL \rightarrow METHY - LI + 1 - O$

74. $METHY - LI + 1 - O \rightarrow LIO + METHANOL$

75. $OOS + METHANOL \rightarrow METHYL - S + OO$

76. $METHYL - S + OO \rightarrow OOS + METHANOL$

77. $OOS + METHANOL \rightarrow METHYL - O + OS$

78. $METHYL - O + OS \rightarrow OOS + METHANOL$

79. $OS + METHANOL \rightarrow METHYL - O + 1 - S$

80. $METHYL - O + 1 - S \rightarrow METHANOL + OS$

81. $OS + METHANOL \rightarrow METHYL - S + 1 - O$

82. $METHYL - S + 1 - O \rightarrow METHANOL + OS$

83. $OOLI + METHANOL \rightarrow METHY - LI + OO$

84. $METHY - LI + OO \rightarrow OOLI + METHANOL$

85. $OOLI + METHANOL \rightarrow METHYL - O + LIO$

86. $METHYL - O + LIO \rightarrow OOLI + METHANOL$

87. $MPLI + METHANOL \rightarrow METHY - LI + MP$

88. $METHY - LI + MP \rightarrow MPLI + METHANOL$

89. $MPLI + METHANOL \rightarrow METHYL - M + PLI$

90. $METHYL - M + PLI \rightarrow MPLI + METHANOL$

91. $MPLI + METHANOL \rightarrow METHYL - P + MLI$

92. $METHYL - P + MLI \rightarrow MPLI + METHANOL$

93. $MLI + METHANOL \rightarrow METHYL - M + 1 - LI$

94. $METHYL - M + 1 - LI \rightarrow MLI + METHANOL$

95. $MLI + METHANOL \rightarrow METHY - LI + 1 - M$

96. $METHY - LI + 1 - M \rightarrow MLI + METHANOL$

General expression for reaction rate is:

$$r = k\left(\frac{T}{T_0}\right)^n \exp[(-E/R)(1/T - 1/T_0)] \prod_{i=1}^{N} C_i^{\alpha i}$$

where r = rate of reaction (kmol/cum sec), k = pre-exponential factor, T_o = reference temperature, T = absolute temperature, n = temperature exponent, E = activation energy, R = Universal gas constant, N = number of reactants involved in the reaction, C_i = concentration of component i and α_i = stoichiometric coefficient of component i

in the reaction equation. Table A.2 presents the values of k and E for above reactions.

Reaction Set A.3: Alkali catalyst removal (fixed conversion of 99.99% is assumed)

$NaOH + H_3PO4 \rightarrow Na_3PO4 + 3\ H_2O$

Reaction Set A.4: Acid catalyst removal (fixed conversion of 99.99% is assumed)

$H_2SO_4 + CAO \rightarrow CASO_4 + H_2O$

Table A.1 Compositions of feed oil (* represents FFAs).

ID	Name	Chemical formula	Compositions of oil
OOO	Triolein	$C_{57}H_{104}O_6$	0.041392286
MMM	Trimyristin	$C_{45}H_{86}O_6$	0.003951082
PPP	Tripalmitin	$C_{51}H_{98}O_6$	0.051834431
PPS	Tag-pps	$C_{53}H_{102}O_6$-13	0.009971778
PPO	Tag-pop	$C_{53}H_{100}$O6-5	0.278645343
POS	Tag-pos	$C_{55}H_{104}O_6$-3	0.046095955
MMP	Tag-mmp	$C_{47}H_{90}O_6$-10	0.015992474
PPLI	Tag-plip	$C_{53}H_{98}O_6$-5	0.086829727
POO	Tag-poo	$C_{55}H_{102}O_6$-6	0.218814675
PLIO	Tag-plio	$C_{55}H_{100}O_6$-7	0.091063029
OOS	Tag-oos	$C_{57}H_{106}O_6$-4	0.021072437
OOLI	Tag-ooli	$C_{57}H_{102}O_6$-5	0.005456256
MPLI	Tag-mlip	$C_{51}H_{94}O_6$-3	0.020696143
MM	1,3-dimyristin	$C_{31}H_{60}O_5$-1	0
PP	1,3-dipalmitin	$C_{35}H_{68}O_5$-1	0.048918156
OO	1,3-diolein	$C_{39}H_{72}O_5$-1	0
PO	Sn-1-palmito-3-olein	$C_{37}H_{70}O_5$-3	0

PLI	Sn-1-palmito-3-linolein	$C_{37}H_{68}O_5$-3	0
MP	Sn-1-myristo-3-palmitin	$C_{33}H_{64}O_5$-7	0
PS	Sn-1-palmito-3-stearin	$C_{37}H_{72}O_5$-7	0
OS	Sn-1-oleo-3-stearin	$C_{39}H_{74}O_5$-4	0
LIO	Sn-1-linoleo-3-olein	$C_{39}H_{70}O_5$-8	0
MLI	Sn-1-myristo-3-linolein	$C_{35}H_{64}O_5$-3	0
1-M	1-monomyristin	$C_{17}H_{34}O_4$	0
1-P	1-monopalmitin	$C_{19}H_{38}O_4$	0
1-S	1-monostearin	$C_{21}H_{42}O_4$	0
1-O	Monoolein	$C_{21}H_{40}O_4$	0
1-LI	1-monolinolein	$C_{21}H_{38}O_4$-1	0
*FFA-O	Oleic acid	$C_{18}H_{34}O_2$	0.02694
*FFA-LiO	Linoleic acid	$C_{18}H_{32}O_2$	0.0066
*FFA-P	Palmitic acid	$C_{16}H_{32}O_2$	0.02562
*FFA-S	Stearic acid	$C_{18}H_{36}O_2$	0.000594
*FFA-M	Myristic acid	$C_{14}H_{28}O_2$	0.00024

Table A.2 k and E for transesterification reactions.

Reaction type	**Reaction no.**	**k (T_o = 323.15 K)** $(kgmol\ K^{-n}/sec\ cum)/(kgmol/cum)^{\Sigma\alpha i}$	**E (kcal/mol)**
TG → DG	1, 7, 13	0.02311	13.5
	19, 29, 37, 45, 57, 59, 61, 63, 65, 67	0.00770	
	21, 31, 39, 47, 55, 77, 85	0.01541	
DG → TG	2, 8, 14, 20, 22, 30, 32, 38, 40, 46, 48, 56, 58, 60, 62, 64, 66, 68, 70, 76, 78, 84, 86, 88, 90, 92	0.001867	10.3
DG → MG	3, 9, 15	0.10659	17.4
	23, 27, 33, 35, 41, 43, 49, 51, 71,	0.05330	

	73, 79, 81, 93, 95		
MG → DG	4, 10, 16, 24, 28, 34, 36, 42, 44, 50, 52, 72, 74, 80, 82, 94, 96	0.002217	16.2
MG → METHYL ESTERS	5,11,17,25,53	0.05754	6.2
METHYL ESTERS → MG	6,12,18,26,54	0.000267	11.9

Table A.3 Important data of selected streams in Figure 3.3, corresponding to the optimal solution ‘‘+’’ in Figure 4.1a; value less than 1×10^{-6} is referred to as trace.

	RFFA1	**W-1-1**	**W-1-2**	**FRAC-2-2**	**D-M-1**	**R-3**	**BIO-D**	**GLYC-OUT**
Temperature (^{o}C)	64.9	172.5	51.4	172.3	65.1	59.5	49.5	50
Pressure (bar)	4	4.1	1	0.22	0.5	4	0.6	0.9
Vapor fraction	0	0	0	0	0	0	0	0
Mass flow rate (kg/h)	16144.18	15094.35	1053.01	15094.35	3028.12	16759.89	15136.23	1632.73
Component mass flow rate (kg/h)								
METHANOL	959.82	7.24	597.39	7.249	1385.13	1570.93	9.13	27.70
OOO	619.08	619.08	trace	619.08	trace	0.056	0.056	0

MMM	59.09	59.094	trace	59.094	trace	< 0.001	< 0.001	trace
METHYL-O	417.36	417.31	0.05	417.31	0.83	5750.12	5750.12	0
GLYCEROL	trace	1.098	367.281	1.098	1562.25	13.13	trace	1562.25
NAOH	0	0	0	0	50.228	90.471	trace	0
WATER	81.3	1.142	70.14	1.142	1.545	0.403	44.708	16.63
H3PO4	0	0	0	0	0	0	0	0
NA3PO4	0	0	0	0	0	0	0	0
PPP	775.25	775.25	trace	775.25	trace	0.091	0.091	trace
METHYL-P	400.69	400.60	0.089	400.60	1.98	7382.67	7382.67	0
PPS	149.14	149.14	0	149.14	trace	0.017	0.017	0
PPO	4167.51	4167.51	0	4167.51	trace	0.25	0.25	trace
POS	689.43	689.43	0	689.43	trace	0.03	0.03	0
MMP	239.19	239.19	0	239.19	trace	0.001	0.001	trace
PPLI	1298.64	1298.64	0	1298.64	trace	0.05	0.05	trace
POO	3272.66	3272.66	0	3272.66	trace	0.21	0.21	trace
PLIO	1361.97	1361.97	0	1361.97	trace	0.045	0.045	0
OOS	315.17	315.17	0	315.17	trace	0.012	0.012	0
OOLI	81.61	81.61	0	81.61	trace	0.033	0.033	0
MPLI	309.54	309.54	0	309.54	trace	0.006	0.006	0
METHYL-M	9.31	9.3	0.005	9.3	0.203	315.94	315.94	0.20
METHYL-S	3.71	3.71	< 0.001	3.71	0.044	401.71	401.71	0.044
METHY-LI	102.28	102.26	0.018	102.26	0.22	1170.05	1170.05	0.22
1-M	0	0	0	0	0.36	0.06	0.06	0.36
1-P	0	0	0	0	2.53	0.86	0.86	2.531
1-S	0	0	0	0	0.076	0.074	0.074	0.076

1-O	0	0	0	0	1.41	1.06	1.06	1.41
1-LI	0	0	0	0	0.193	0.21	0.21	0.193
MM	0	0	0	0	trace	0.001	0.001	trace
PP	731.63	731.63	0.003	731.63	< 0.001	0.15	0.15	< 0.001
OO	0	0	0	0	< 0.001	0.13	0.13	< 0.001
PO	0	0	0	0	< 0.001	0.29	0.29	< 0.001
PLI	0	0	0	0	< 0.001	0.057	0.057	< 0.001
MP	0	0	0	0	< 0.001	0.017	0.017	< 0.001
PS	0	0	0	0	trace	0.02	0.02	trace
OS	0	0	0	0	trace	0.018	0.018	trace
LIO	0	0	0	0	trace	0.051	0.051	trace
MLI	0	0	0	0	trace	0.003	0.003	trace
FFA-O	5.31	5.30	0.005	5.30	0.006	5.29	5.29	0.006
FFA-L-O	1.3	1.29	0.002	1.29	0.002	1.29	1.29	0.002
FFA-P	3.27	3.26	0.006	3.26	0.007	3.26	3.26	0.007
FFA-S	0.047	0.047	< 0.001	0.047	< 0.001	0.047	0.047	< 0.001
FFA-M	0.12	0.12	0.001	0.12	0.001	0.12	0.12	0.001
H2SO4	89.73	71.71	18.01	71.71	21.09	50.61	48.06	21.10
CASO4	0	0	0	0	0	0	0	0
CAO	0	0	0	0	0	0	0	0

Table A.4 Important data of selected streams in Figure 3.4, corresponding to the optimal solution ‘‘+’’ in Figure 4.3a; value less than 1×10^{-6} is referred to as trace.

	RFFA1	WASH-1-1	WASH-1-2	RTRANS1	WASH-2-1	WASH-2-2	BIO-D	GLYC-OUT	UNRE-OIL
Temperature (^{o}C)	64.4	54.9	54	60	30	39	140.3	103.9	245
Pressure (bar)	4	1	1	4	1	1	0.9	0.2	1
Vapor fraction	0	0	0	0	0	0	0	0	0
Mass flow rate (kg/h)	16227.48	15273.61	1322.26	19125.95	15189.55	1887.93	14868.92	1590.67	287.41
Component mass flow rate (kg/h)									
METHANOL	955.93	120.23	835.70	2250.59	3.28	19.22	Trace	0.36	trace
OOO	505.35	505.35	trace	3.46	3.46	trace			3.53
MMM	62.32	62.32	trace	0.33	0.33	trace			0.33
METHYL-O	311.72	311.64	0.084	5503.27	5503.25	0.014	5497.75	0.009	5.57
GLYCEROL	trace	2.547	365.832	1558.482	trace	1558.482	0	1558.482	0
NAOH	trace	trace	trace	139.637	trace	139.637	0	0.14	Trace
WATER	89.96	0.28	89.68	0.81	31.46	148.96	trace	22.67	Trace
H3PO4	0	0	0	0	0	0	0	0.12	0
NA3PO4	0	0	0	0	0	0	0	0	0
PPP	671.04	671.04	trace	5.27	5.27	trace			5.38
METHYL-P	154.66	154.59	0.07	7050.12	7050.09	0.03	7050.04	0.006	0.016
PPS	157.69	157.69	trace	1.22	1.22	trace	0	0	1.24
PPO	4102.87	4102.87	trace	25.83	25.83	trace	0	0	26.29
POS	727.78	727.78	trace	4.49	4.49	trace	0	0	4.57
MMP	252.31	252.31	trace	1.37	1.37	trace	0	0	1.40
PPLI	1370.59	1370.59	trace	8.14	8.14	trace	0	0	8.28
POO	3306.51	3306.51	trace	20.67	20.67	trace	0	0	21.04

PLIO	1286.08	1286.08	trace	4.892	4.89	trace	0	0	4.96
OOS	332.66	332.66	trace	2.015	2.01	trace	0	0	2.05
OOLI	86.56	86.56	trace	0.938	0.93	trace	0	0	0.96
MPLI	326.6	326.6	trace	1.86	1.86	trace	0	0	1.89
METHYL-M	154.81	154.63	0.175	476.28	476.27	0.01	475.80	0.001	trace
METHYL-S	156.25	156.22	0.031	573.96	573.96	0.001	572.62	< 0.001	1.35
METHY-LI	154.96	154.90	0.056	1225.04	1225.03	0.006	1224.53	0.004	0.503
1-M	5.75	4.94	0.81	5.73	5.66	0.07	< 0.001	0.07	5.75
1-P	66.69	62.59	4.10	65.72	65.51	0.21	trace	0.21	66.69
1-S	6.81	6.634	0.176	6.696	6.691	0.006	trace	0.006	6.81
1-O	66.77	64.46	2.31	65.61	65.51	0.11	trace	0.11	66.77
1-LI	14.51	14.13	0.37	14.29	14.26	0.022	trace	0.022	14.50
MM	0.13	0.13	trace	0.13	0.13	trace	0	trace	0.13
PP	775.25	775.24	0.01	7.59	7.59	trace	0	trace	7.75
OO	5.022	5.022	< 0.001	4.90	4.90	trace	0	trace	5.02
PO	13.16	13.16	< 0.001	12.87	12.87	trace	0	trace	13.16
PLI	2.85	2.85	< 0.001	2.79	2.79	trace	0	trace	2.85
MP	1.04	1.04	< 0.001	1.03	1.03	trace	0	trace	1.05
PS	1.17	1.17	trace	1.14	1.14	trace	0		1.17
OS	1.10	1.10	trace	1.07	1.07	trace	0		1.10
LIO	1.88	1.88	trace	1.84	1.84	trace	0	trace	1.88
MLI	0.23	0.23	trace	0.22	0.22	trace	0	trace	0.23
FFA-O	3.52	3.51	0.007	3.51	3.51	< 0.001	0.324	< 0.001	0.005
FFA-L-O	1.76	1.76	0.005	1.761	1.761	< 0.001	0.508	< 0.001	1.276
FFA-P	0.97	0.96	0.004	0.96	0.96	< 0.001	0.96	< 0.001	0.005
FFA-S	1.77	1.77	0.003	1.77	1.77	< 0.001	0.007	< 0.001	1.80
FFA-M	1.74	1.73	0.015	1.73	1.73	< 0.001	1.73	< 0.001	< 0.001
H2SO4	88.57	65.77	22.80	65.77	44.62	21.15	44.61	8.46	0.02
CASO4	0	0	0	0	0	0	0	0	0

CAO	0	0	0	0	0	0	0	0	0
N2	0	0	0	0	0	0	0	0	0

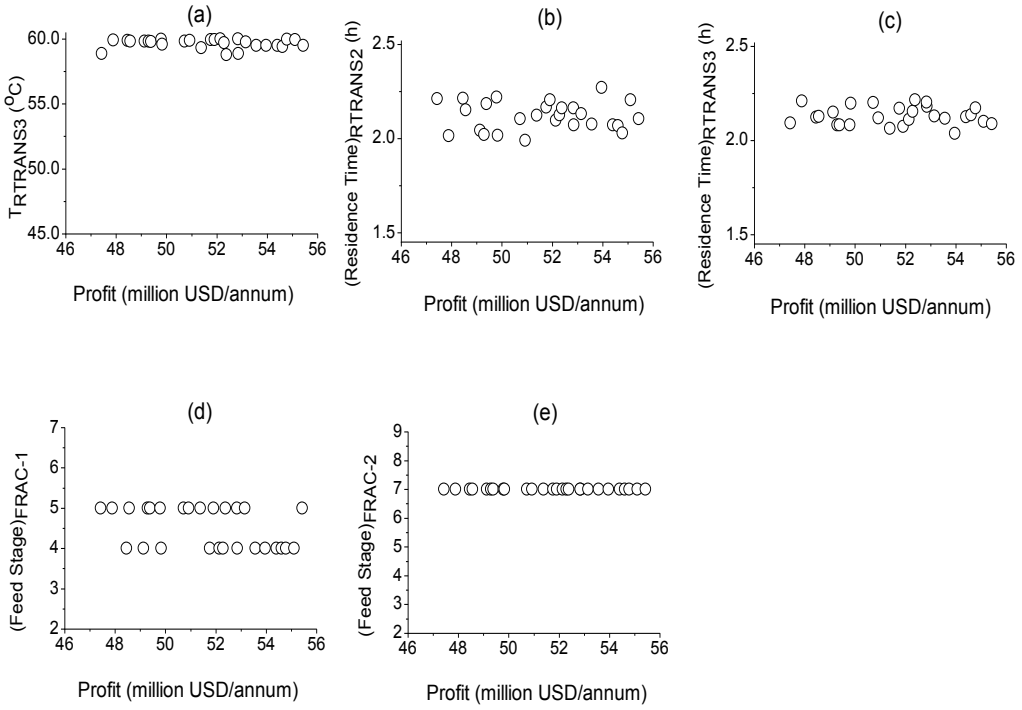

Figure A.1 Optimal values of some decision variables from the simultaneous maximization of profit and minimization of heat duty for Process 1.

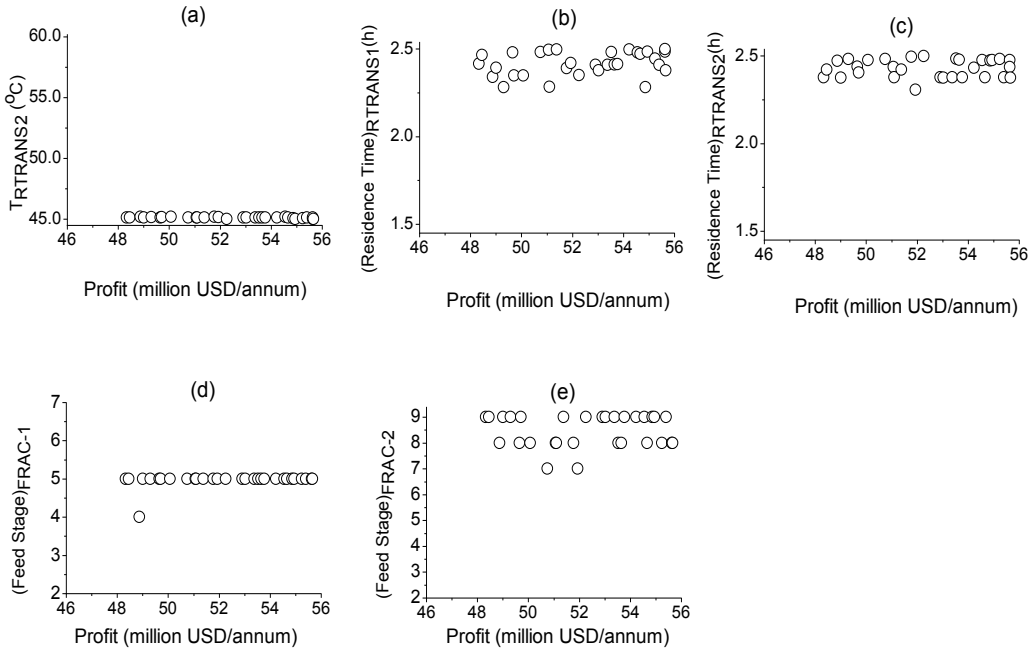

Figure A.2 Optimal values of some decision variables from the simultaneous maximization of profit and minimization of organic waste for Process 1.

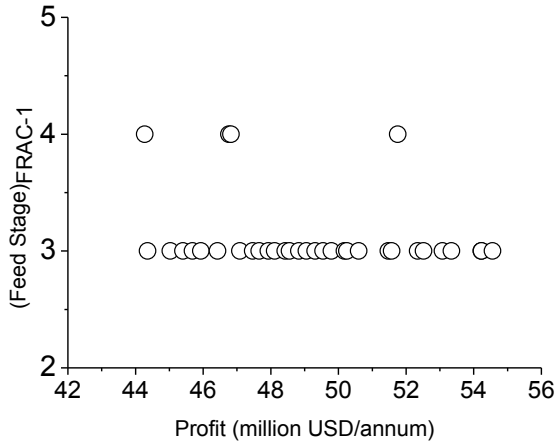

Figure A.3 Optimal values of $(\text{Feed Stage})_{\text{FRAC-1}}$ from the simultaneous maximization of profit and minimization of heat duty for Process 2.

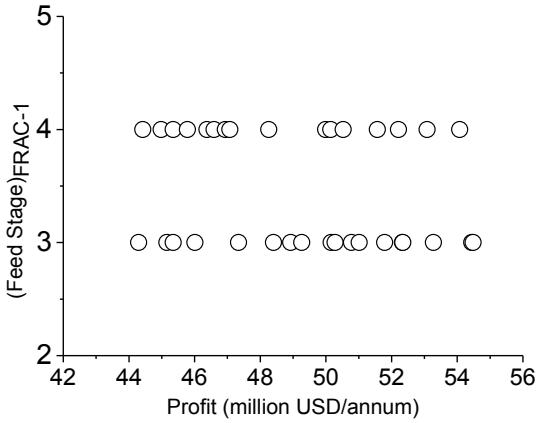

Figure A.4 Optimal values of $(\text{Feed Stage})_{\text{FRAC-1}}$ from the simultaneous maximization of profit and minimization of organic waste for Process 2.

APPENDIX B

Table B.1 'Downs Drill' Table Indicating Component Material Balances[a].

Component	Input (streams)	Generation (+)[a]	Output [-] (streams)	Consumption [-][a]	Accumulation (inventory) controlled by
Oil (TG+DG+MG+FFA)	OIL	Some reactions in reaction Sets S1 and S2	WASTE and BIO-D	Some reactions in reaction Set A.1 and A.2	Feed oil flow control [FC100]
Methanol	MEOH and MEOH-1	Some reactions in reaction Sets S1 and S2	ME-WAT-1, WASTE and BIO-D	Some reactions in reaction Set A.1 and A.2	Methanol/(TG+DG+MG) and methanol/FFA ratio [RC100 and RC200]
Sodium hydroxide	NAOH	0	0	Reaction Set A.3	Sodium hydroxide/(TG+DG+MG) ratio control [RC201]
Phosphoric acid	H3PO4 and H3PO4-2	0	0	Reaction Set A.3	pH control [pH200 and pH201]
Sulfuric acid	H2SO4	0	0	Reaction Set A.4	Sulfuric acid /FFA ratio control [RC101]
Calcium oxide	CAO	0	0	Reaction Set A.4	pH control [pH100]
Water	WATER	Reaction Sets S3 and	WASTE	0	Wash water flowrate control

		S4			[CC200]
Calcium sulphate	0	Reaction Set S4	CASO4	0	pH control [pH100]
Sodium phosphate	0	Reaction Set S3	NA3PO4 and NA3PO4-2	0	pH control [pH200 and pH 201]
FAME	0	Some reactions in reaction Sets S1 and S2	BIO-D	Some reactions in reaction Set A.1 and A.2	Methanol/(TG+DG+MG) and methanol/FFA ratio [RC100 and RC200]
Glycerol	0	Some reactions in reaction Set S2	GLYC-OUT and WASTE	Some reactions in reaction Set A.2	Methanol/(TG+DG+MG) [RC200]

[a]Numbers shown in parentheses refer to the controller in Figure 3.9 in the main paper.

APPENDIX C

C.1 FRAC3 startup

```
Task colstartup Runs at 0

// Ensure that controllers are in manual

  Blocks("PC").Automan: 1;

  Blocks("LC1").Automan: 1;

  Blocks("TC").Automan: 1;

  Blocks("LC2").Automan: 1;

// Start the column reflux

  Blocks("FRAC3").Reflux.FmR: 0.0;

// Add some feed to the column

  Blocks("FC").Automan: 0;

  Blocks("FC").SP: 16793.9;

// Wait for the sump level to reach 2.6m and then turn off the column feed

  wait for Blocks("LC2").PV >= 2.6;

  Blocks("FC").SP: 0;

// Put the pressure controller into auto & enter the set point

  Blocks("PC").Automan: 0;

  Blocks("PC").SP: 0.34;

// Open the colum vent valve to purge the nitrogen

  Blocks("VVENT").pos: 100;

// Increase reboiler steam temperature gradually

  Blocks("TC").OPMan: 100;
```

```
  Wait 0.1;
  Blocks("TC").OPMan: 150;
  Wait 0.1;
  Blocks("TC").OPMan: 200;
  Wait 0.1;
// Start the column reflux
  Blocks("FRAC3").Reflux.FmR: 770;
  Wait 0.05;
// Continue increasing steam temperature
  Blocks("TC").OPMan: 230;
// Close vent valve when N2 is purged
  Blocks("VVENT").pos: 0;
// Put the reflux drum level control into auto & enter the set point
  Blocks("LC1").Automan: 0;
  Blocks("LC1").SP: 0.33;
// Add some more feed until the sump level reaches 2.6m
  Blocks("FC").SP: 16793.9;
  wait for Blocks("LC2").PV >= 2.6;
  Blocks("FC").SP: 0;
// Increase reboiler steam temp
  Blocks("TC").OPMan: 250;
  wait 0.15;
  Blocks("TC").OPMan: 280;
```

wait 0.15;

// Wait until the level in the reflux drum rises to 0.3

wait for Blocks("LC1").PV >= 0.3;

// ... put the sump level controller to automatic

Blocks("LC2").Automan: 0;

Blocks("LC2").SP: 2.4;

// and increase the reflux rate to the final value

Blocks("FRAC3").Reflux.FmR: 777.621;

// start the column feed - put the feed valve to 50% open

Blocks("FC").SP: 16793.9;

wait 0.5;

// Ramp up the steam temperature

Blocks("TC").OPMan: 320;

// Wait until bottom temperature reaches 230 ^{O}C and put the temperature controller to Auto mode

wait for Blocks("TC").PV >= 230;

Blocks("TC").Automan: 0;

wait 0.1;

// Change the reflux level & sump level set points to the final value

Blocks("LC1").SP: 0.36;

Blocks("LC2").SP: 1.64;

// Wait for 1 more hour and pause the simulation

wait 1.0;

Pause;

End

C.2 Utility trip in FRAC3

Task utilitytrip

Runs When Blocks("FRAC3").TReb >= 250;

Blocks("TC").OPMan: 100;

Print "UTILITYTRIP encountered due to reboiler temperature shoot up";

pause;

End

APPENDIX D

Hazard and Operability Study (HAZOP) Report for Homogeneously Catalyzed Biodiesel Production from WCO

Glossary and Abbreviations

HAZARDS AND OPERABILITY STUDIES (HAZOP)	A formal systematic critical examination to the process and engineering intentions of new or existing facilities to assess the hazard potential of any maloperation or malfunction of any equipment and their ramifications on the facility.
DEVIATION	A departure from design and operating intentions.
GUIDE WORDS	All possible deviations from design and operating intentions are tries to be visualized during the critical examination.
HAZARD	A deviation which may cause damage, injury or other form of loss.
STUDY TEAM	A group of people carrying out this investigation.
EIS	Environmental Impact Statement
PHA	Preliminary Hazard Analysis
FHA	Final Hazard Analysis
FMEA	Failure Modes and Effects Analysis
P&ID	Process and Instrumentation Diagram

Summary

As per our resources, a preliminary HAZOP analysis for biodiesel production from WCO (Figure 3.9) is carried out to inderstand the risks associated with the process. HAZOP analysis is one of the important analyses, viz. construction safety, fire safety, FHA, transport, emergency plan, and safety management system. The objective of this analysis is to systematically examine the proposed design, which should be done before the physical construction. Possible hazards and operational

problems can be prevented or reduced by redesign of suitable operating procedures. Plant items in the process flowsheet are evaluated by applying appropriate guide words. Potentially hazardous situations and their ramifications are then estimated. Preventing measures to avoid or reduce the undesirable situations are also recommended. The findings of the step by step procedure and the recommendations are organized in the HAZOP minute sheet. Figure 3.17 presents HAZOPed process diagram for biodiesel production from WCO. The important recommendations from this analysis are:

The vital recommendations from this analysis are:

Rec #1

Install high flow alarm on feed line.

Rec #10, #24, #52 & #60

Install high level alarms on the column to ensure that the operating efficiency is maintained by avoiding the flooding of reboiler outlet.

Rec #8, #16, #22, #30, #34, #42, #50, #56, #58, #64, #66

Install high pressure and high temperature alarms on columns and reactors to prevent overheating.

Rec #15, #29, #57 & #65

Investigate the need for protection against such back into the column on cooling.

Hazop Study

Technical description of the plant and the guide words and any other important details are explained briefly to enable reader to follow the minute sheets.

1.1 Description of the facility

The main plant items consist of distillation columns (FRAC-1, FRAC-2, FRAC-3, FRAC-4), Four CSTRs (RFFA, RTRANS1, RTRANS2, RTRANS3). Heat exchangers (H-1, H-3), Coolers (H-2, H-4, H-5), phase separators (W-1, D-1, D-2, WASH-2) and pumps and control instruments. A process description has been given in the earlier section (see Figure 3.9). The control structure obtained by applying a systematic integrated framework approach is discussed in the previous section.

1.2 HAZOP team members

Normally, a team should consist of experts from all relevant fields from design through commissioning to operation (design engineer, operation engineer, maintenance supervisor, HAZOP chairman and instrument engineer. However in this study, a preliminary analysis is carried out by us.

1.3 HAZOP methodology

All important unit operations in the plant are HAZOPed. Guide words such as HIGH FLOW, as described below, are used in the minute sheet. For each guide word, the potential causes were analyzed and mentioned in the second column. Their ramifications are mentioned in the third column. The fourth column is to record any existing design or operational safeguards. The recommendations, for the causes which may lead to several hazardous situation or loss in terms of product and time, are then entered in the sixth column against the recommendation number (Rec #). These recommendations include possible changes to the system to eliminate or reduce the consequences. Further evaluation is considered necessary as required and the recommendations are minuted accordingly.

1.4 Guide words

The guide words used in this analysis are:

Flow: HIGH LOW ZERO REVERSE

Level: HIGH LOW

Pressure: HIGH LOW

Temperature: HIGH LOW

1.5 Plant overview

In this analysis, only the operating mode is covered. However, in a complete HAZOP study including start-up/shutdown procedures, more changes may be recommended. The issue to be analysed further prior to changing the design are:

Rec #17, #25, #65 & #73

Consider nitrogen gas purging in the distillation columns (and in condensers) before start-up, to expel air sucked in on cooling during shut down.

Rec #16, #24, #64 & #72

Recommendations minuted (regarding backup cooling water system) to be adopted or not; further investigations may be needed.

1.5 Analysis of main findings

The HAZOP results are described in the minute sheet (Table D.1). The results of each deviation are examined to verify if the ramification would cause a hazardous condition to the plant. All critical unit operations are analysed. If the hazard or loss is found to be credible, the safeguard should be developed to eliminate or reduce the possibility. Additionally, the alarms and trip systems are recommended wherever the possibilities of hazard are anticipated. Please refer to the minute sheet.

1.6 Action arising from HAZOP study

The recommendations outlined from the HAZOP analysis that are to be included in the design are as shown in Figure 3.18 (Drawing no. BD 001 REV2). Note the changes and the additional instruments and alarms.

The implementation of the changes as a result of HAZOP should not lead to any potential hazard to plant personnel, public or environment.

The pre-commissioning and commissioning checklists and the test procedures should be modified to ensure that the final recommendations of HAZOP are verified at every appropriate stage.

Table D.1 HAZOP minute sheet.

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *OIL*		Page no.:	
Node Description: *Feed line*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Flow	*Flow controller fault*	*Increase in reactors, phase separators and columns level after some limit.* *Temperature will fall down.* *Reactor duty and reboiler duty will try to maintain the temperatures until capacity is reached.* *Eventually, flooding in the reactors and columns will occur, and column will stop operating.* *Although the adverse consequences are unlikely, poor operation of the plant can be avoided.*		*1*	*Independent (of controller FC100) high flow alarm on 'OIL' stream.*		

Low Flow	*Feed pump failed; Isolating valve jammed*	*Temperature rise in reactors and columns i.e. overheating. Drop in the liquid level in the equipments. Not Severe*					
Zero Flow	*As above*	*As above*	*Emergency shut down*				

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *W-1*		Page no.:	
Node Description: *Phase separator*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault. Malfunction of upstream operations including line/valve blockages.*	*Overflow in W-1 (upper layer).*		*2*	*Independent (of controller LC101) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream operations.*	*Not severe issue.*		*3*	*Low level alarm on LC101.*		
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in W-1 (lower layer).*		*4*	*Independent (of controller LC102) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream operations.*	*Not severe issue.*		*5*	*Low level alarm on LC102.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *RFFA*		Page no.:	
Node Description: *Esterification reactor*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level/ Low Level	*Level controller fault*	*Overflow in RFFA/Not severe.*		*6*	*Independent (of controller LC100) high level alarm/ Low level alarm on LC100.*		
High Pressure	*Fire*	*Equipment damage.*		*7*	*PSV.*		
High Temperature	*Controller malfunction or feed loss*	*Liquid vaporization.*		*8*	*High temperature alarm on TC100.*		
Low Temperature	*Controller malfunction*	*Not severe but loss of conversion*		*9*	*Low temperature alarm on TC100.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *FRAC-1*		Page no.:	
Node Description: *Distillation columns*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault*	*Flooding and reboiler operation stops.*		*10*	*Independent (of controller LC106) high level alarm. An independent alarm above the normal control level can alert the operator to take early action.*		
Low Level	*Controller malfunction or low flow*	*Not severe issue*		*11*	*Low level alarm on LC106. This will ensure early operator intervention to prevent product loss.*		
High Level	*Level controller fault*	*Overflow. High pressure in condenser.*		*12*	*Independent (of controller LC105) high level alarm.*		
Low Level	*Controller malfunction or low flow*	*Pump 'P-4' damage due to running dry.*		*13*	*Low level alarm on LC105. No flow switch on pump would protect the pump against dry operation. PSV*		
High Pressure	*Controller malfunction or water failure in condenser*	*Pressure rise. Condenser vent is needed.*		*14*	*Pressure indicator on FRAC-1. High pressure alarm on PC102. Backup cooling water. Thermocouple on vent.*		

					Consider reorientation of water.		
Reverse Flow	*Cooling of condenser and column after shutdown.*	*Suck back of air into column on cooling.* *Although air sucking may not be a severe issue as no explosive material is present in column, possibility of corrosion should be checked.*		*15*	*Consider nitrogen purging.*		
High Temperature	*Controller malfunction or loss of feed*	*Glycerol decomposition above 150^{o}C in FRAC-1.*		*16*	*High temperature alarm on TC102.*		
Low Temperature	*Controller malfunction*	*Not severe.*		*17*	*Low temperature alarm on TC102.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *R-CAO*		Page no.:	
Node Description: *Neutralization reactor*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in R-CAO.*		*18*	*Independent (of controller LC107) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream operations.*	*Not severe issue.*		*19*	*Low level alarm on LC107.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *F-1*		Page no.:	
Node Description: *Flash*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault. Malfunction of upstream operations.*	*Rise in level in F-1. Over pressurization.*		*20*	*Independent (of controller LC108) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream operations.*	*Not severe issue.*		*21*	*Low level alarm on LC108.*		
High Pressure	*Controller malfunction*	*Pressure rise on F-1.*		*22*	*Pressure indicator on F-1 on PC103. High pressure alarm. PSV*		
Low Pressure	*Controller malfunction.*	*Low pressure. Liquid vaporization.*		*23*	*Low pressure alarm on PC100.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *FRAC-2*		Page no.:	
Node Description: *Distillation column*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault*	*Flooding and reboiler operation stops.*		*24*	*Independent (of controller LC104) high level alarm. An independent alarm above the normal control level can alert the operator to take early action.*		
Low Level	*Controller malfunction or low flow*	*Not severe issue*		*25*	*Low level alarm on LC104. This will ensure early operator intervention to prevent product loss.*		
High Level	*Level controller fault*	*Overflow. High pressure in condenser.*		*26*	*Independent (of controller LC103) high level alarm.*		
Low Level	*Controller malfunction or low flow*	*Pump 'P-3 damage due to running dry.*		*27*	*Low level alarm on LC105 & LC103. No flow switch on pump would protect the pump against dry operation.*		
High Pressure	*Controller malfunction or water failure in condenser*	*Pressure rise. Condenser vent is needed.*		*28*	*Pressure indicator on FRAC-2. High pressure alarm on PC101. Backup cooling water. Thermocouple on vent.*		

					Consider reorientation of water. *PSV*		
Reverse Flow	*Cooling of condenser and column after shutdown.*	*Suck back of air into column on cooling.* *Although air sucking may not be a severe issue as no explosive material is present in column, possibility of corrosion should be checked.*		*29*	*Consider nitrogen purging.*		
High Temperature	*Controller malfunction or loss of feed*	*Biodiesel decomposition above 250^{o}C FRAC-2.*		*30*	*High temperature alarm on TC101.*		
Low Temperature	*Controller malfunction*	*Not severe.*		*31*	*Low temperature alarm on TC101.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *RTRANS1*		Page no.:	
Node Description: *Transesterification reactor*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Leve/Low Level	*Level controller fault/ low flow or Pump 'P-12' failure.*	*Overflow in RTRANS1/Not severe.*		*32*	*Independent (of controller LC200) high level alarm/ Low level alarm on LC200.*		
High Pressure	*Fire*	*Equipment damage.*		*33*	*PSV.*		
High Temperature	*Controller malfunction or feed loss*	*Liquid vaporization.*		*34*	*High temperature alarm on TC200.*		
Low Temperature	*Controller malfunction*	*Not severe but loss of conversion*		*35*	*Low temperature alarm on TC200.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *D-1*		Page no.:	
Node Description: *Phase separator*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in D-1 (upper layer).*		*36*	*Independent (of controller LC201) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream operations.*	*Not severe issue.*		*37*	*Low level alarm on LC201.*		
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in D-1 (lower layer).*		*38*	*Independent (of controller LC202) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream*	*Not severe issue.*		*39*	*Low level alarm on LC202.*		

	operations.						

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *RTRANS2*		Page no.:	
Node Description: *Transesterification reactor*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Leve/Low Level	*Level controller fault/ low flow*	*Overflow in RTRANS2/Not severe*		*40*	*Independent (of controller LC203) high level alarm/ Low level alarm on LC203.*		
High Pressure	*Fire*	*Equipment damage.*		*41*	*PSV.*		
High Temperature	*Controller malfunction or feed loss*	*Liquid vaporization.*		*42*	*High temperature alarm on TC201.*		
Low Temperature	*Controller malfunction*	*Not severe but loss of conversion*		*43*	*Low temperature alarm on TC201.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *D-2*		Page no.:	
Node Description: *Phase separator*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in D-2 (upper layer).*		*44*	*Independent (of controller LC204) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream operations.*	*Not severe issue.*		*45*	*Low level alarm on LC204.*		
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in D-2 (lower layer).*		*46*	*Independent (of controller LC205) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream*	*Not severe issue.*		*47*	*Low level alarm on LC205.*		

	operations.						

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *RTRANS3*		Page no.:	
Node Description: *Transesterification reactor*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level/ Low Level	*Level controller fault/low flow*	*Overflow in RTRANS3/Not severe.*		*48*	*Independent (of controller LC206) high level alarm/ Low level alarm on LC206.*		
High Pressure	*Fire*	*Equipment damage.*		*7*	*PSV.*		
High Temperature	*Controller malfunction or feed loss*	*Liquid vaporization.*		*50*	*High temperature alarm on TC202.*		
Low Temperature	*Controller malfunction*	*Not severe but loss of conversion*		*51*	*Low temperature alarm on TC202.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *FRAC-3*		Page no.:	
Node Description: *Distillation column*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault*	*Flooding and reboiler operation stops.*		*52*	*Independent (of controller LC211) high level alarm. An independent alarm above the normal control level can alert the operator to take early action.*		
Low Level	*Controller malfunction or low flow*	*Not severe issue*		*53*	*Low level alarm on LC211. This will ensure early operator intervention to prevent product loss.*		
High Level	*Level controller fault*	*Overflow. High pressure in condenser.*		*54*	*Independent (of controller LC210) high level alarm.*		
Low Level	*Controller malfunction or low flow*	*Pump 'P-9' damage due to running dry.*		*55*	*Low level alarm on LC210. No flow switch on pump would protect the pump against dry operation.*		
High Pressure	*Controller malfunction or water failure in condenser*	*Pressure rise. Condenser vent is needed.*		*56*	*Pressure indicator on FRAC-3. High pressure alarm on PC204. Backup cooling water. Thermocouple on vent. Consider reorientation of*		

					water. *PSV*		
Reverse Flow	*Cooling of condenser and column after shutdown.*	*Suck back of air into column on cooling.* *Although air sucking may not be a severe issue as no explosive material is present in column, possibility of corrosion should be checked.*		*57*	*Consider nitrogen purging.*		
High Temperature	*Controller malfunction or loss of feed*	*Biodiesel decomposition above 250^{o}C.*		*58*	*High temperature alarm on TC204.*		
Low Temperature	*Controller malfunction*	*Not severe.*		*59*	*Low temperature alarm on TC204.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *FRAC-4*		Page no.:	
Node Description: *Distillation column*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault*	*Flooding and reboiler operation stops.*		*60*	*Independent (of controller LC208) high level alarm. An independent alarm above the normal control level can alert the operator to take early action.*		
Low Level	*Controller malfunction or low flow*	*Not severe issue.*		*61*	*Low level alarm on LC208. This will ensure early operator intervention to prevent product loss.*		
High Level	*Level controller fault*	*Overflow. High pressure in condenser.*		*62*	*Independent (of controller LC207) high level alarm.*		
Low Level	*Controller malfunction or low flow*	*Pump 'P-8' damage due to running dry.*		*63*	*Low level alarm on LC207. No flow switch on pump would protect the pump against dry operation.*		
High Pressure	*Controller malfunction or water failure in condenser*	*Pressure rise. Condenser vent is needed.*		*64*	*Pressure indicator on FRAC-4. High pressure alarm on PC203. Backup cooling water. Thermocouple on vent. Consider reorientation of*		

					water. *PSV*		
Reverse Flow	*Cooling of condenser and column after shutdown.*	*Suck back of air into column on cooling.* *Although air sucking may not be a severe issue as no explosive material is present in column, possibility of corrosion should be checked.*		*65*	*Consider nitrogen purging.*		
High Temperature	*Controller malfunction or loss of feed*	*Glycerol decomposition above 150^{o}C.*		*66*	*High temperature alarm on TC203.*		
Low Temperature	*Controller malfunction*	*Not severe.*		*67*	*Low temperature alarm on TC203.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *R-CAT2*		Page no.:	
Node Description: *Neutralization reactor*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault.* *Malfunction of upstream operations.*	*Overflow in R-CAT2.*		*68*	*Independent (of controller LC209) high level alarm.*		
Low Level	*Controller malfunction or low flow.* *Malfunction of upstream operations.*	*Not severe issue.*		*69*	*Low level alarm on LC209.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *R-CAT*		Page no.:	
Node Description: *Neutralization reactor*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault.* *Malfunction of upstream operations.*	*Overflow in R-CAT.*		*70*	*Independent (of controller LC212) high level alarm.*		
Low Level	*Controller malfunction or low flow.* *Malfunction of upstream operations.*	*Not severe issue.*		*71*	*Low level alarm on LC212.*		

BIODIESEL PRODUCTION FROM WCO **HAZOP MINUTE SHEET**

Project: *Homogeneously catalysed biodiesel production from WCO*				Node: *WASH-2*		Page no.:	
Node Description: *Phase separator*						Date: --	
						Drw No.: *BD 001 REV1*	
GUIDEWORD	CAUSE (S)	CONSEQUENCE (S)	SAFEGUARD	REC#	RECOMMENDATION (S)	INDIV	ACTION
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in WASH-2 (upper layer).*		*72*	*Independent (of controller LC213) high level alarm.*		
Low Level	*Controller malfunction or low flow. Malfunction of upstream operations.*	*Not severe issue unless pump runs dry.*		*73*	*Low level alarm on LC213. No flow switch on pump would protect the pump against dry operation.*		
High Level	*Level controller fault. Malfunction of upstream operations.*	*Overflow in WASH-2 (lower layer).*		*74*	*Independent (of controller LC214) high level alarm.*		
Low Level	*Controller malfunction or low flow.*	*Not severe issue unless pump runs dry.*		*75*	*Low level alarm on LC214. No flow switch on pump would protect the pump against dry*		

	Malfunction of upstream operations.				*operation.*		

LIST OF PUBLICATIONS

Journals:

1. Patle, D. S., Wei P. E. & Ahmad, Z. (2015). Simulation and economic analysis of biodiesel production using supercritical methanol. **Journal of Engineering Science, Journal of Engineering Science**, 11, 17–26.
2. Patle, D. S., Ahmad, Z., & Rangaiah, G. P. (2015). Multi-loop control system design for biodiesel process using waste cooking oil. **Journal of Physics: Conference Series,** (In press).
3. Patle, D. S., Ahmad, Z., & Rangaiah, G. P. (2014). Plantwide control of biodiesel production from waste cooking oil using integrated framework of simulation and heuristics, **Industrial & Engineering Chemistry Research, ACS,** 53 (37), 14408-14418.(**IF: 2.24)**
4. Patle, D. S., Sharma, S., Ahmad, Z., & Rangaiah, G. P. (2014). Multi-objective optimization of two alkali catalyzed processes for bio-diesel from waste cooking oil. **Energy Conversion and Management, Elsevier,** 85, 361-372. **(IF: 3.6)**
5. Patle, D. S., Ahmad, Z., & Rangaiah, G. P. (2014). Operator training simulator in chemical industry: review, issues and future directions. **Reviews in Chemical Engineering**, **De Gruyter,** 30(2), 199-216.(**IF: 2.83)**
6. Patle, D. S., & Ahmad, Z. (2014). Techno-economic analysis of an alkali catalyzed biodiesel production using waste palm oil. **Applied Mechanics and Materials,** 465-466, 120-124.(**Scopus)**

Manuscripts under Preparation:

1. Patle, D. S., Ahmad, Z., Rangaiah, G. P., Operator training simulator for a homogeniously alkali catalyzed biodiesel production from waste cooking oil. (under review).

Conference Proceedings:

1. Patle, D. S., Ahmad, Z., & Rangaiah, G. P. (2014). Biodiesel production from waste cooking oil: plant-wide control system design using integrated framework approach, 5th International Symposium on Advanced Control of Industrial Processes, Hiroshima, Japan, May 28-30, 2014.
2. Patle, D. S., & Ahmad, Z. (2013). Training simulator development for palm oil based biodiesel production plant, Proceedings of the 6th International Conference on Process Systems Engineering (PSE ASIA), Kuala Lumpur, June 25-27, 2013.
3. Patle, D. S., & Ahmad, Z. (2012). Simulation, cost and energy analysis of eco-friendly biodiesel production plant, International Conference on Environment 2012 (ICENV 2012), Penang, Malaysia, December 11-13, 2012.